UNESCO/IUPAC Postgraduate Course in Polymer Science

Lecture:

Polymer Morphology

Miroslav Šlouf

Institute of Macromolecular Chemistry ASCR, Heyrovsky sq. 2, Prague -162 06

http://www.imc.cas.cz/unesco/index.html

unesco.course@imc.cas.cz

Polymer Morphology

Miroslav Šlouf
Group of Polymer morphology
Department of Polymer materials
Institute of Macromolecular Chemistry AS CR

1) Why is polymer morphology important?	
	Examples: morphology-properties relationships.
	Structures, microstructures, nanostructures, molecules, atoms...
2) Which methods do we use in polymer morphology?	
	Microscopic methods: LM, SEM, TEM...
	Other methods: diffraction, thermic, rheological, scanning probe...
3) Which polymer structures and systems are usually studied?	
	Homopolymers (amorphous, semicrytalline, crystals).
	Copolymers (block copolymers, other types of copolymers).
	Polymer blends (compatibility, structure and properties, recycling).
	Polymer composites (microcomposites, nanocomposites, dispersion).
	Special cases (liquid crystalline polymers, hydrogels, polymer particles...)

Why polymer morphology?

Basic facts and definitions.

Morphology

(1) a ***study of structure*** or form

(2) a ***structure***, form

Polymer morphology

(1) a ***study of structure*** or polymers

(2) a ***structure*** of polymers

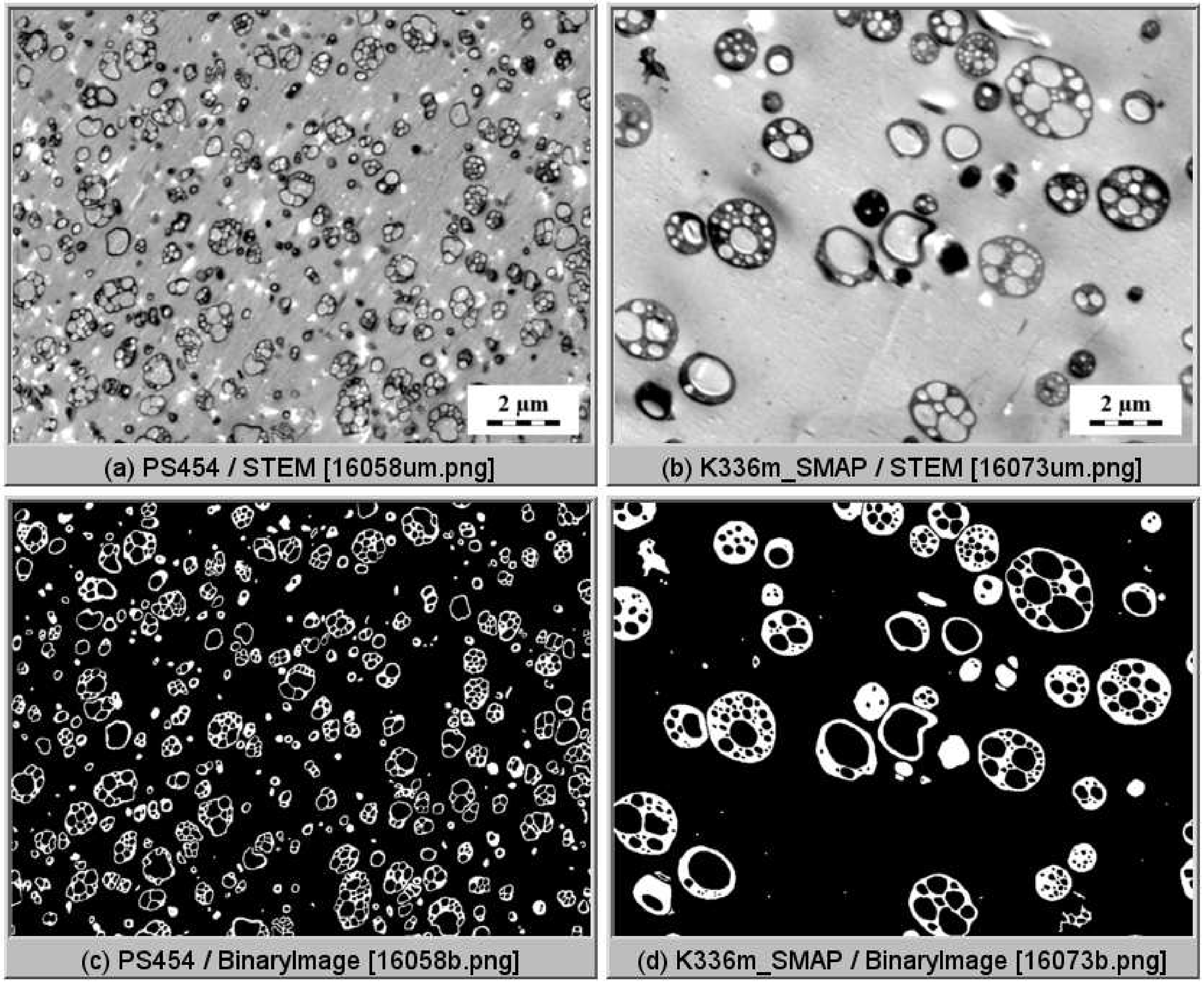
Note: the term *polymer morphology* is (usually) connected with solid state
the term *polymer rheology* is (always) connected with molten state
the term *polymer structure* is (often) connected with molecular structure

---

Structure = (a) structure in general or (b) structure with dimensions 1mm and more
Microstructure = structures with dimensions 1μm...1000μm
Nanostructure = structures with dimensions 1nm...1000nm
Phase structure = structure of system containing several phases (composite, blend)
Supermolecular structure = structures of higher order than molecular structures
Molecular structure = structure of molecules (primary, secondary, tertiary...)
Atomic structure = (a) structure of molecules or (b) structure of atoms

Why polymer morphology?

Example1, part1: morphology of HIPS.



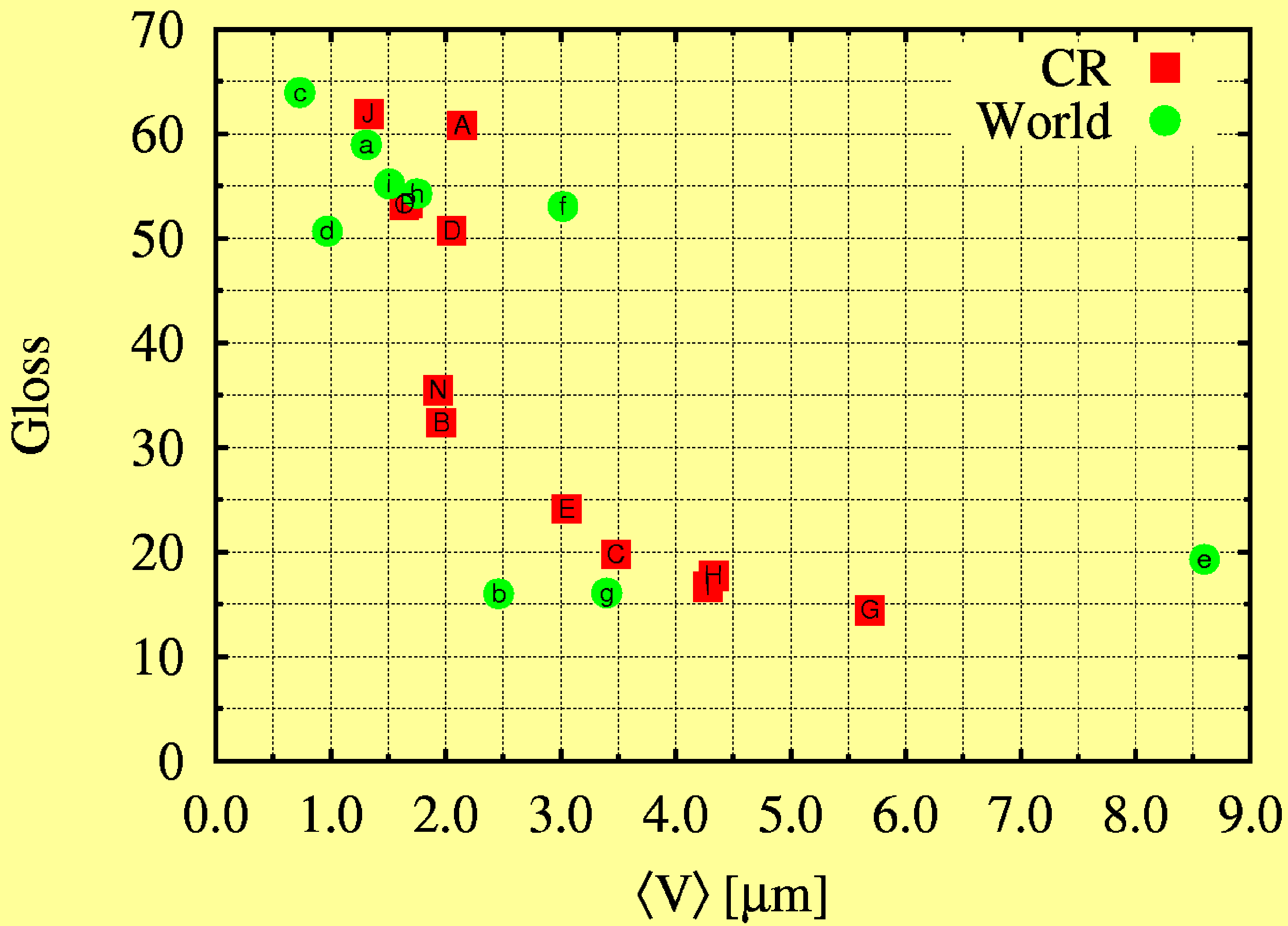
Notes:

1) HIPS is a common copolymer of PS and BP.
2) Year production of PS ≈ 20 megatonnes.
3) From 1960, more than 50% of PS is in the form of HIPS.
4) All HIPS polymers have approximately the same chemical composition.
5) HIPS morphology is strongly influenced by processing technology.

STEM micrographs and binary images of various high-impact polystyrenes.

Why polymer morphology?

Example1, part2: properties of HIPS.



Conclusion:

1) All points in the graph represent high-impact polystyrenes (HIPS) with more-or-less the same chemical composition.

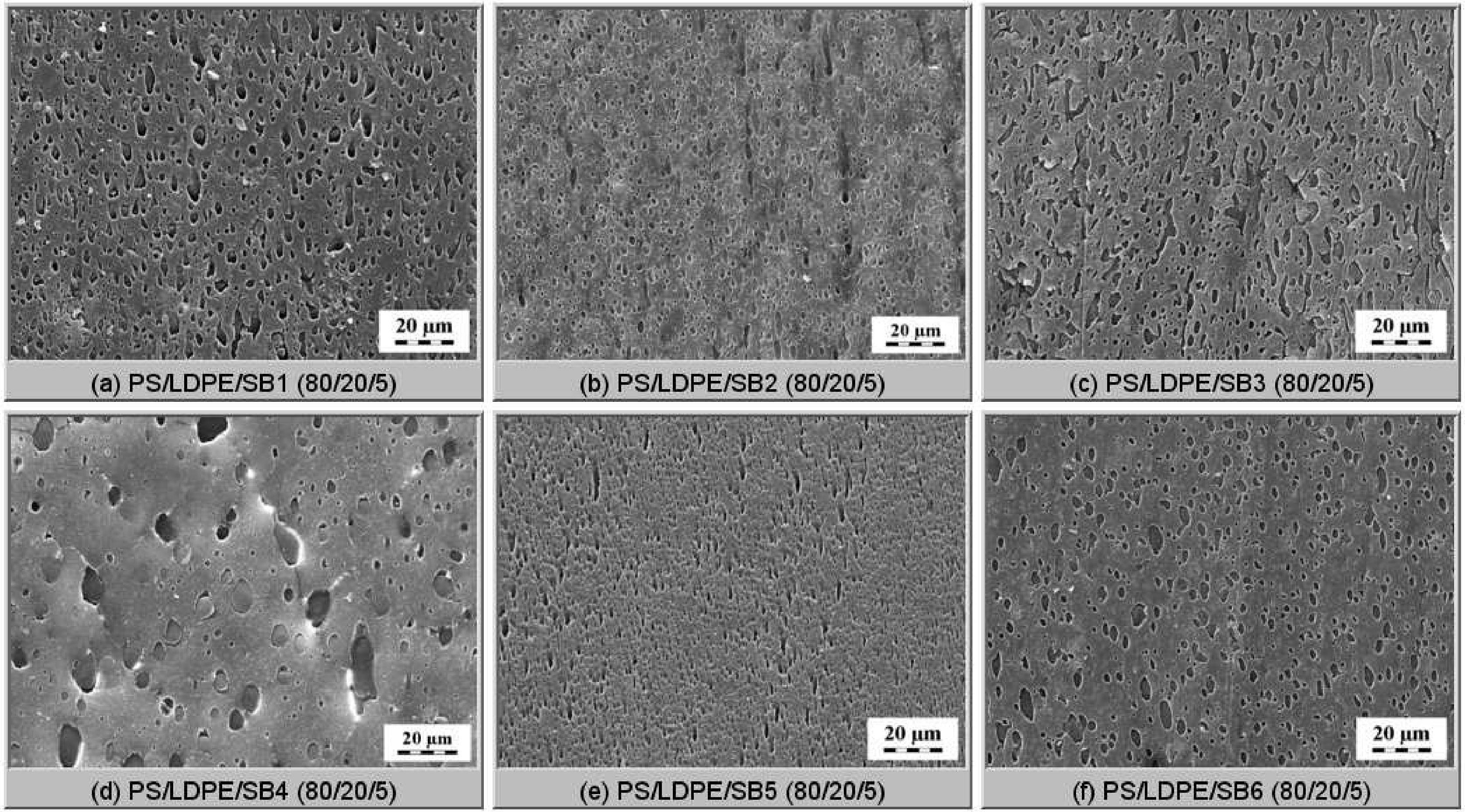
2) Gloss of HIPS is drastically influenced by its morphology.

Gloss of high-impact polystyrenes as a function of particle size.

Source: research report for company SYNTHOS, group of Polymer Morphology.

Why polymer morphology?

Example2, part1: morphology of PS/LDPE/SBx polymer blends.



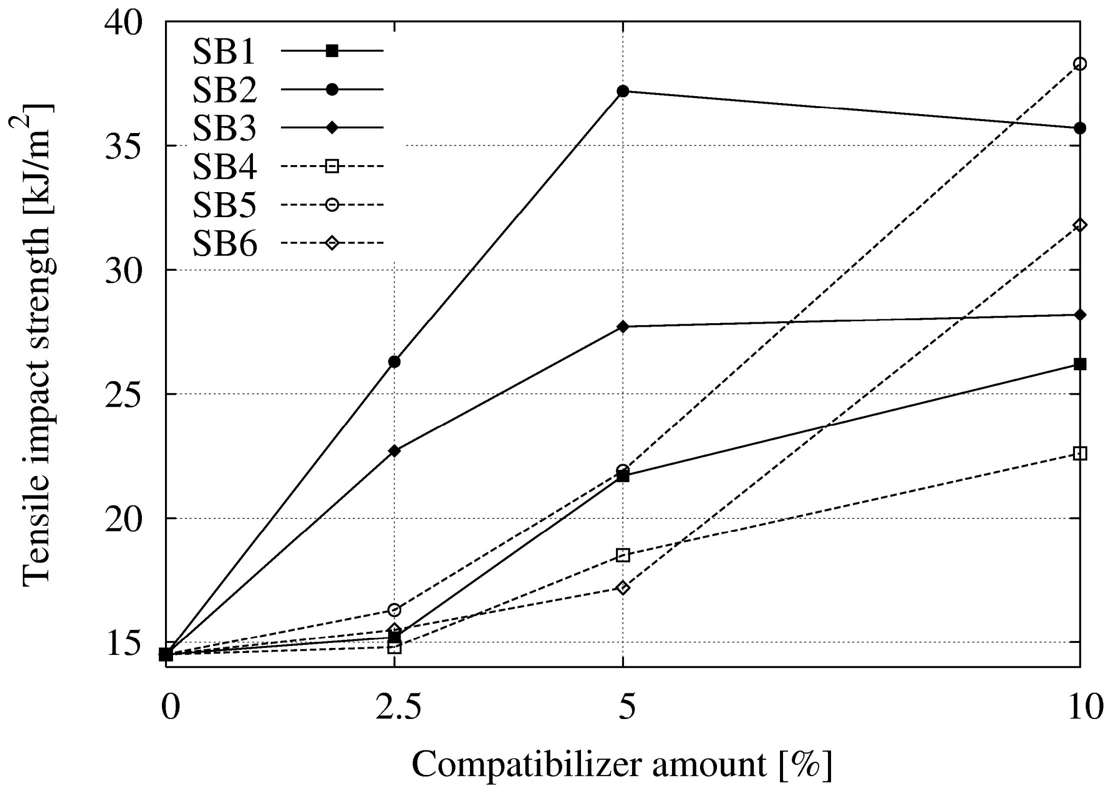
SEM/SE micrographs showing morphology of PS/LDPE/SBx (80/20/5) blends.

PS = polystyrene, LDPE = low-density polyethylene.

SBx = various types of styrene-budadiene compatibilizers (x = 1..6).

Why polymer morphology?

Example2, part2: properties of PS/LDPE/SBx polymer blends.



Conclusion:

1) All PS/LDPE/SBx blends have almost identical chemical composition (80/20 + 5% of SBx); only compatibilizers SBx are different styrene-butadiene block copolymers (x=1,2,3,4,5,6).

2) Morphology and impact strength of PS/LDPE/SBx is strongly influenced by compatibilizer.

Impact strength of PS/LDPE/SBx (80/20/5) as a function of SBx concentrations.

Source: Fortelny I, Slouf M et al. *J. Appl. Pol. Sci.*100 (2005) 2803–2816.

Why polymer morphology?

Structures, microstructures, nanostructures and atoms.

Dimensions in microworld

Light microscopy					Special+LS				LM
Scanning electron microscopy							FESEM		SEM
		Transmission electron microscopy						HRTEM+ED	TEM
		Atomic force microscopy / Scanning probe microscopy						STM	SPM
					SAXS			WAXS	XRD
10	1	0.1	0.01	0.001	0.0001	0.00001	0.000001	0.0000001	mm
10000	1000	100	10	1	0.1	0.01	0.001	0.0001	um
10000000	1000000	100000	10000	1000	100	10	1	0.1	nm
structure		microstructure			nanostructure			atoms	structure

Microscopic methods (LM, SEM, TEM, SPM):	..focused on microstructure and nanostructure
Diffraction/scattering methods (XRD, ND, ED, LS):	..focused on nanostructure and atomic structure
Spectroscopic methods (IR, NMR, ESR...):	..focused on atomic/molecular structures
Other methods (thermal, mechanical testing...):	..focused on properties, rather than structure

(according to MŠ)

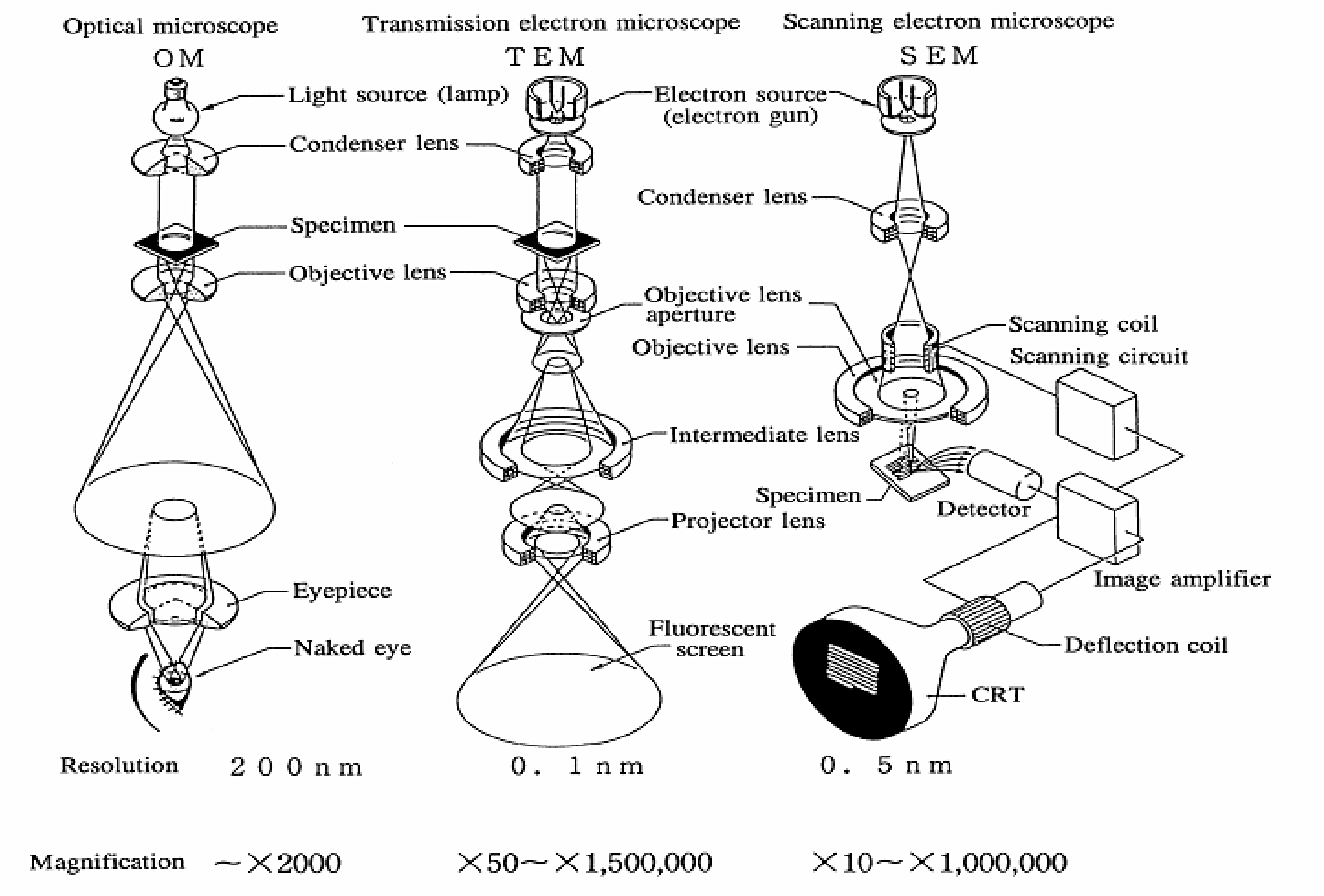
Why polymer morphology?

Examples of typical synthetic polymer structures = morphologies.

Selected structures/morphologies of synthetic polymers	Methods
Homopolymer microparticles (latex microspheres... 100-10um)	LM, SEM
Semicrystalline polymers, spherulites (100-10um)	LM, SEM
Liquid crystalline polymers, textures (100-10um)	PLM (SEM)
Polymer microcomposites (filler particles 100-1um)	LM, SEM
Polymer blends (inhomogeneities 10-0.1um)	SEM, STEM, TEM
Semicrystalline polymers - single lamellae (10um-10nm)	SEM, TEM, SWAXS
Block copolymers (domain size 100-10nm)	TEM (SEM, SPM)
Polymer nanocoposites (filler particles 100-1nm)	TEM
Polymer nanoparticles (nanospheres, micelles... 100-1nm)	TEM
Polymer molecules (random coils... 10-1nm)	LS, SAXS (SPM)
Polymer single crystals, atomic structure (0.1nm)	HRTEM, ED, WAXS
Decrease in size →	(according to MŠ)

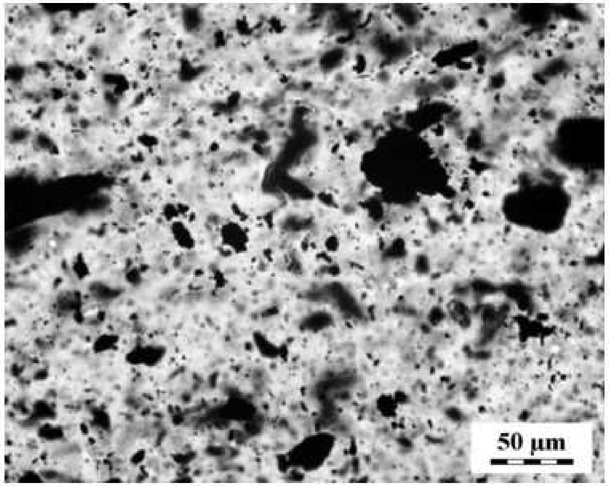
Methods of polymer morphology.

(Standard, classic) microscopic methods.

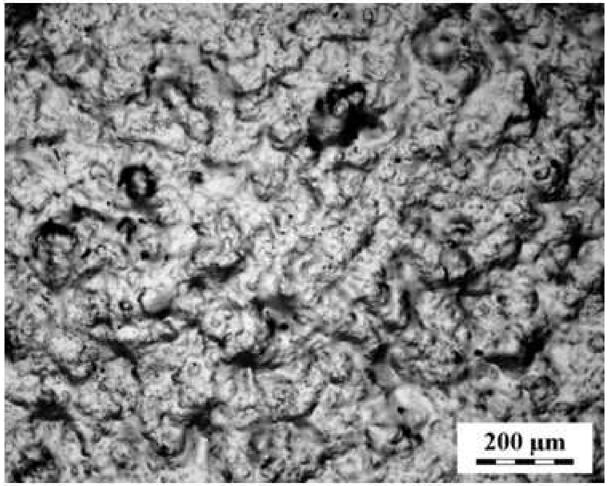


Methods of polymer morphology.

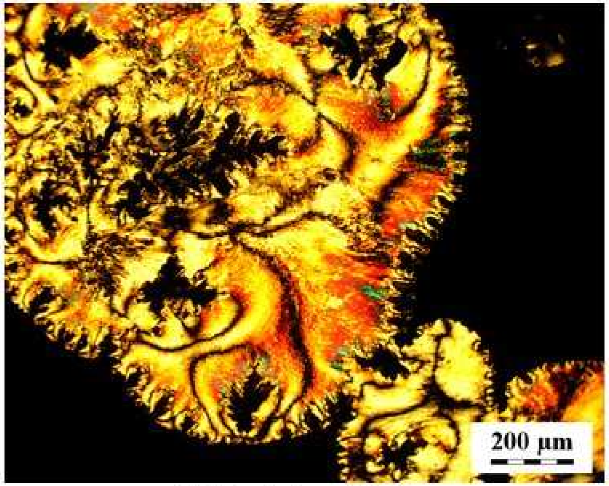
LM = light microscopy: the most common modes.



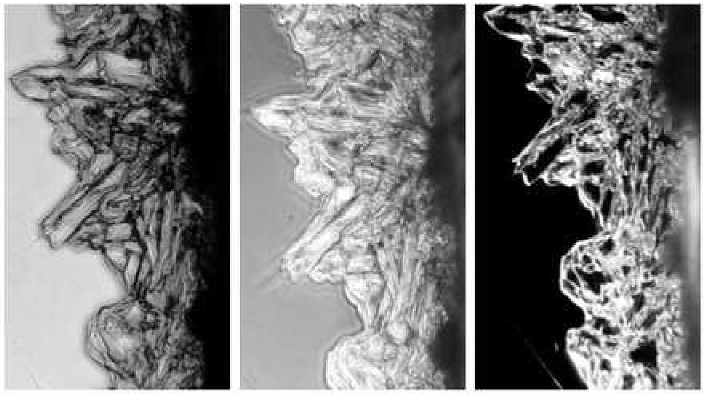
LM/transmitted light:
thin section of PMMA/CNT(1%) composite



LM/reflected light:
surface of Epoxy/SiO2 composite



LM/polarized light:
melted layer of polymer liquid crystal



LM/BrightField/PhaseContrast/DarkField:
LM/BF + LM/PC + LM/DF of saccharose crystals

LM in transmitted light
$\Rightarrow$ internal morphology

LM in reflected light
$\Rightarrow$ surface morphology

PLM polarized light microscopy
$\Rightarrow$ sample anisotropy

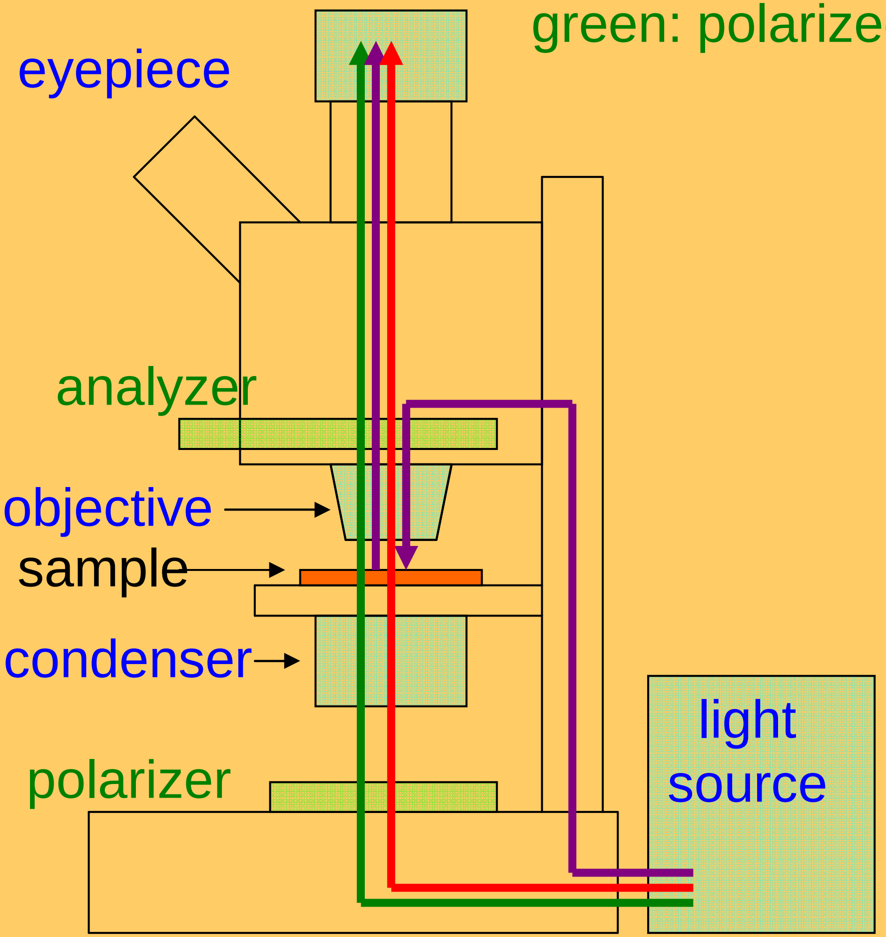
Other modes
special contrast
special applications

Methods of polymer morphology.

LM: simplified scheme of microscope.

Light microscope

red: transmitted light
violet: reflected light
green: polarized light



Simple explanation of light polarization.

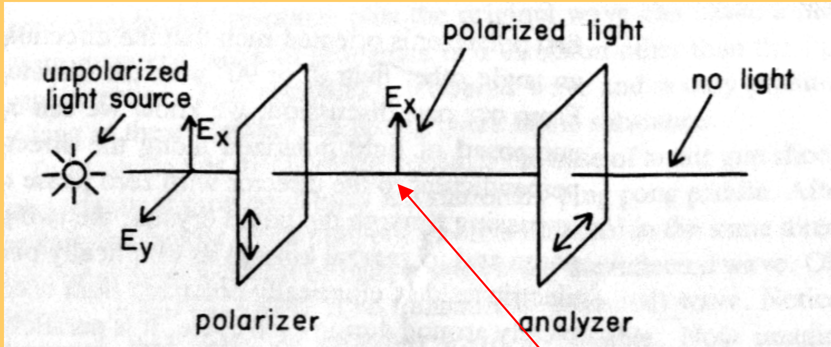


Fig. 4.10 The effect of a crossed polarizer and analyzer. The polarizer allows only light polarized along the *x*-axis to pass, while the analyzer allows only light polarized along the *y*-axis to pass. Since there is no light polarized along the *y*-axis emerging from the polarizer, no light passes through the analyzer.

What happens if we put sample here?

no sample ⇒ dark

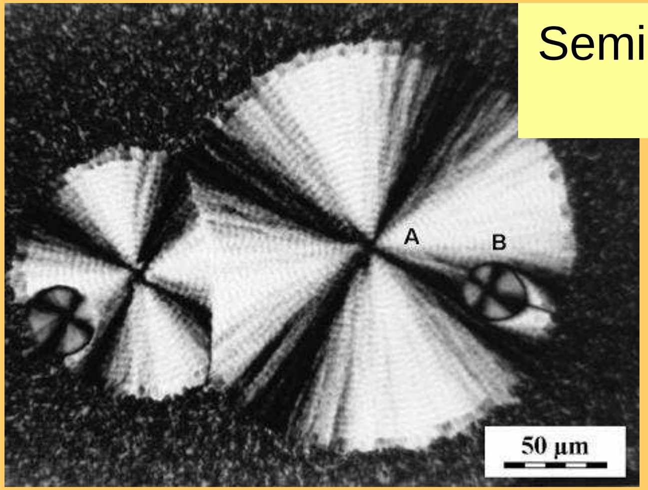
isotropic material ⇒ dark

anisotropic material ⇒ light

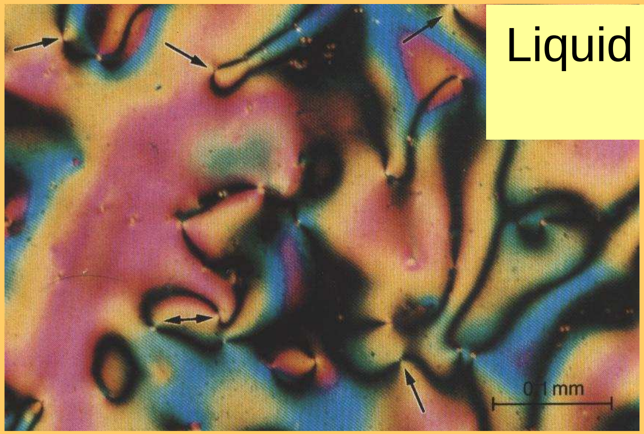
Methods of polymer morphology.

LM: typical applications and synthetic polymer morphologies.

Polarized light = PLM =
the most important mode
in polymer morphology.

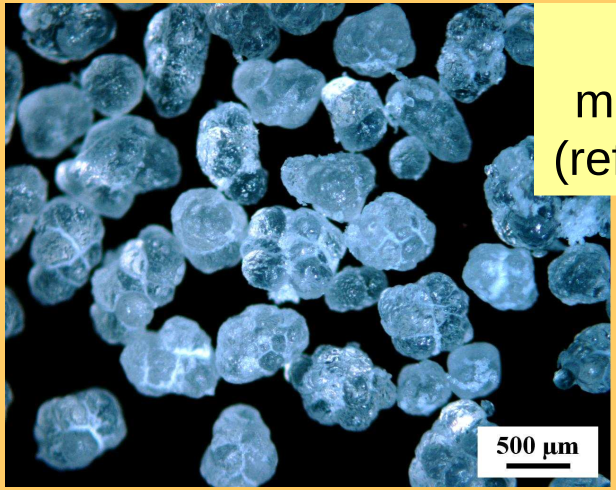


Semicrystalline polymers



Liquid crystalline polymers

Transmitted and reflected light.
basic modes, important in biology,
but also in polymers, material science...

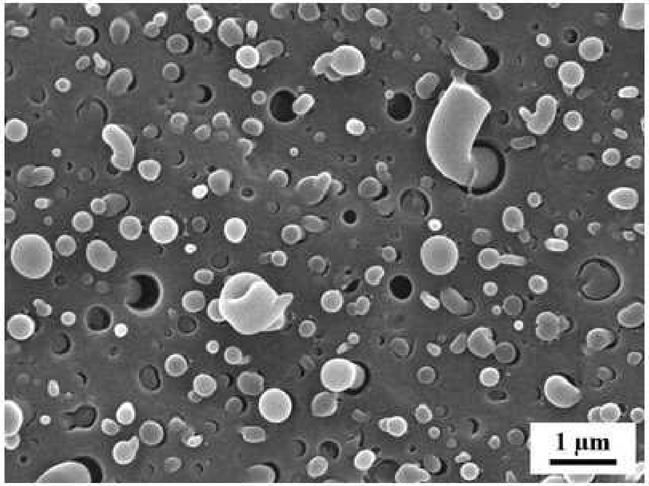


Polymer microparticles (reflected light)

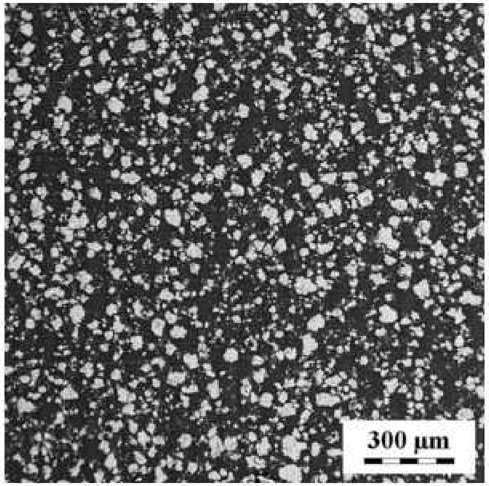
Polymer capsules with medicament in H_2O (transmitted light)

Methods of polymer morphology.

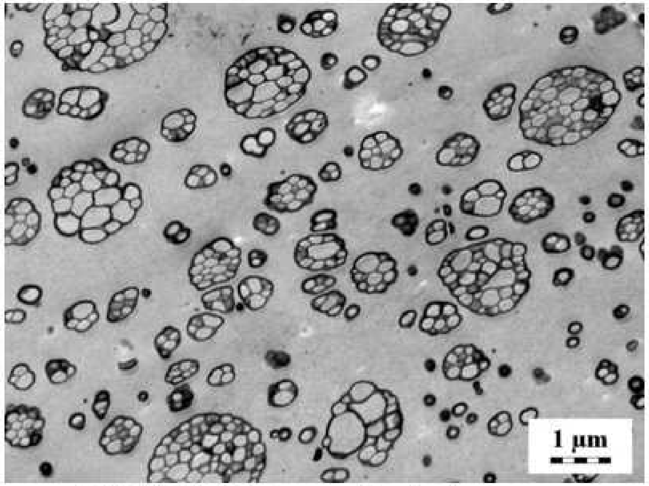
SEM = scanning electron microscopy: the most common modes.



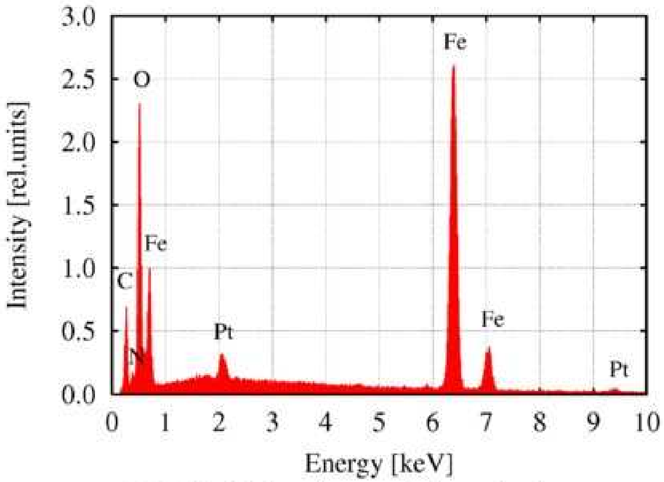
SEM/SE: topographic contrast
in PP/COC blend (fracture surface)



SEM/BSE: material contrast
in Epoxy/ATH composite (smooth surface)



SEM/STEM: transmitted electrons
in HIPS polymer (ultrathin section)



SEM/EDX: elemental analysis
of magnetic polymer microspeheres

SEM/SE
(secondary electrons)
⇒ surface morphology
(also inner surfaces!
(breaking, cutting...

SEM/BSE
(backscattered electrons)
⇒ composition
(light × heavy elements

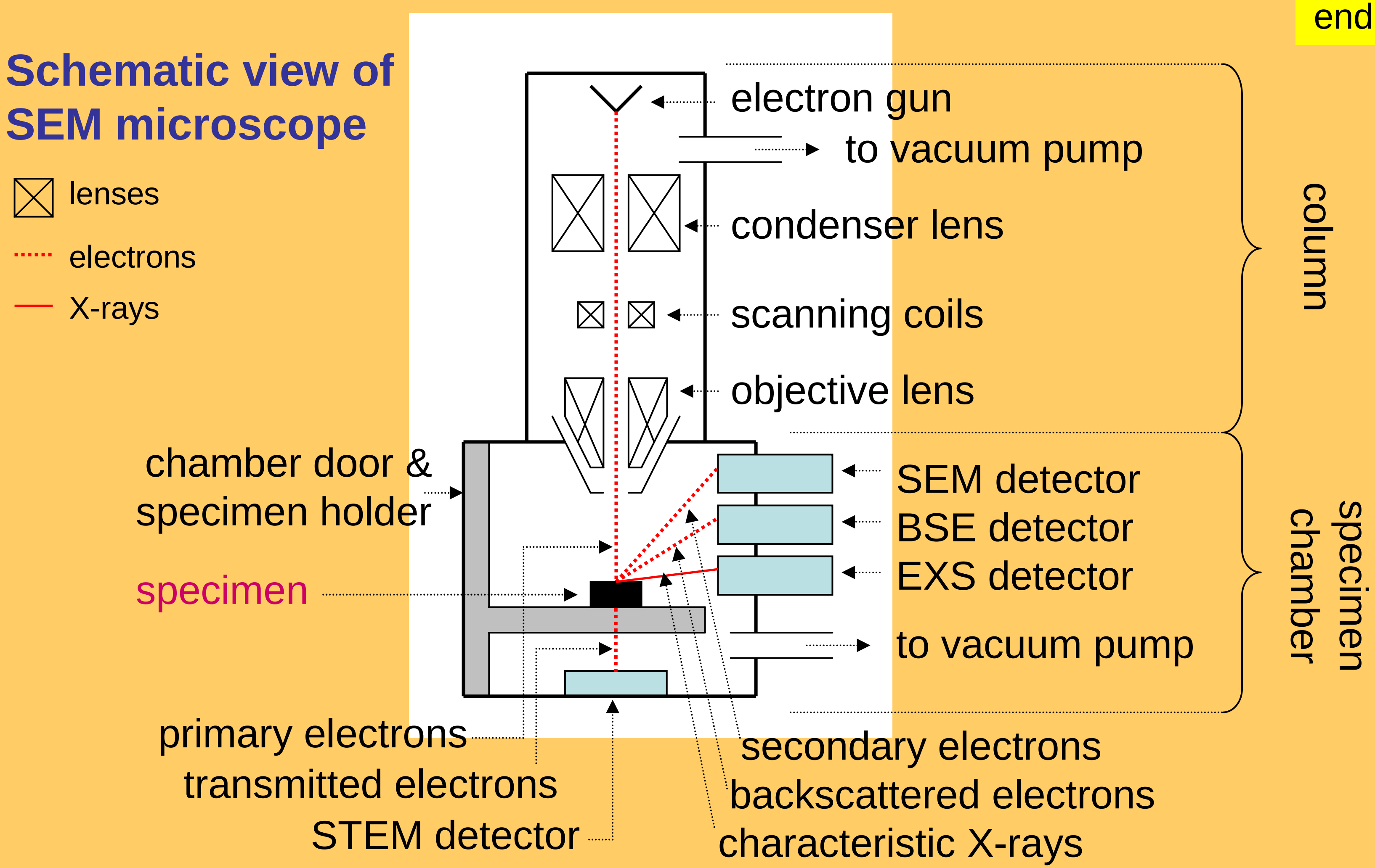
SEM/STEM
(transmitted electrons)
⇒ internal structure
(light × heavy elements

SEM/EDX
(characteristic X-rays)
⇒ elemental analysis
(precision issues!
(detection limits
(resolution

Methods of polymer morphology.

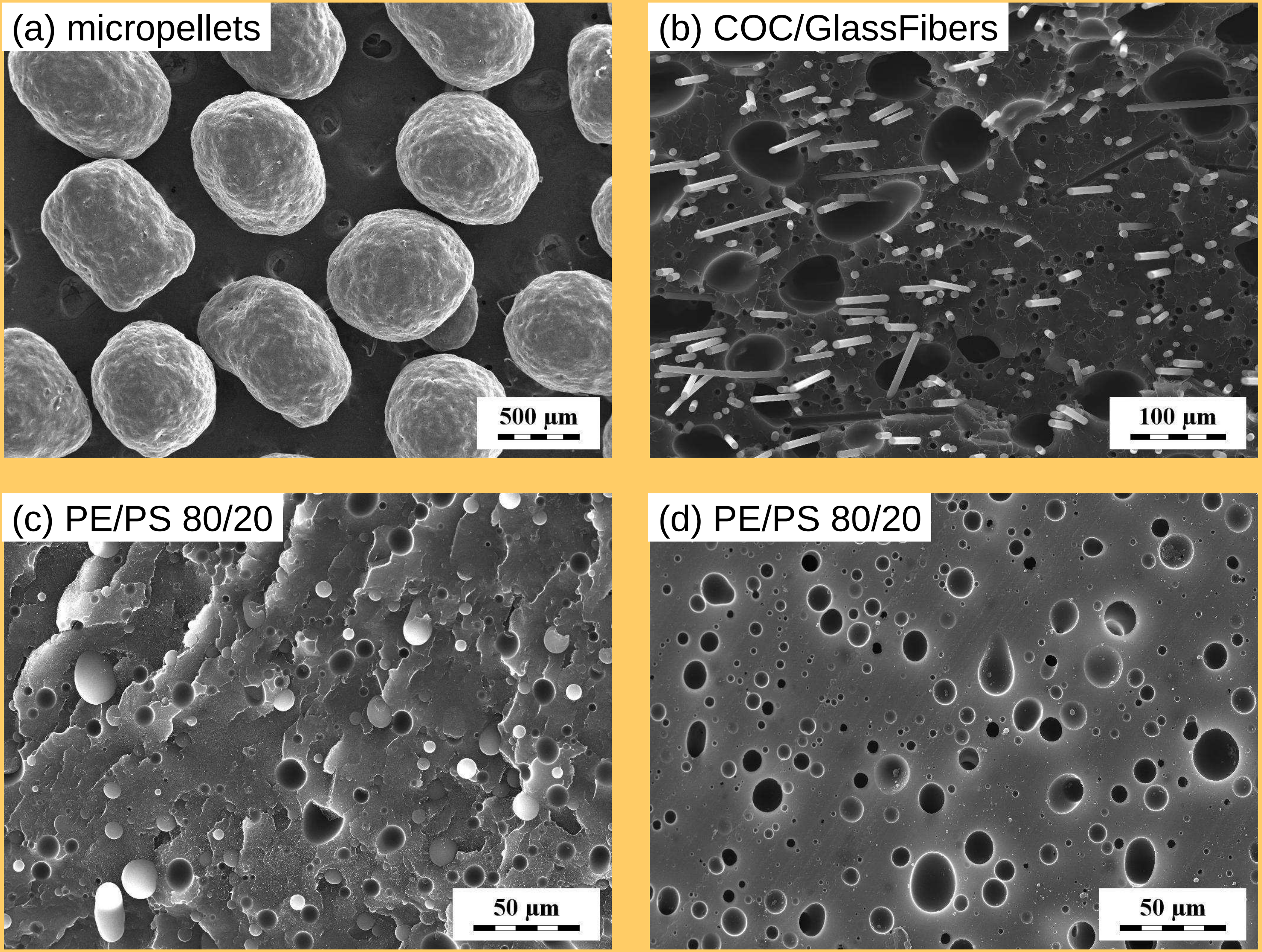
SEM: simplified scheme of microscope.

More details end of lecture



Methods of polymer morphology.

SEM: typical applications in polymer morphology.



Typical mode:
SEM/SE (>90%)

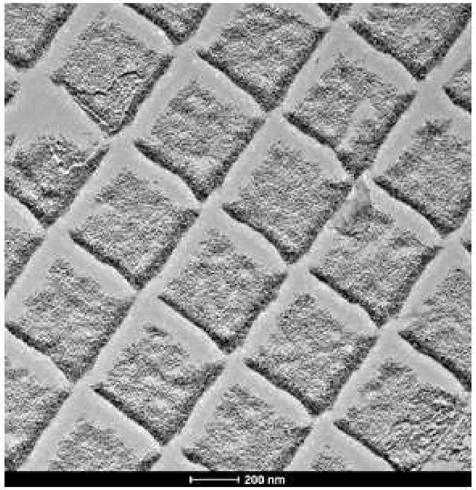
Typical apps in polymer science:
(a) microparticles
(b) microcoposites
(c-d) blends

Typical sample preparation:
a) just fix+observe
...mostly used for micropowders
b-c) fracture in liquid nitrogen
...mostly used for polymer blends and composites
d) smooth+etch
...mostly used for polymer blends

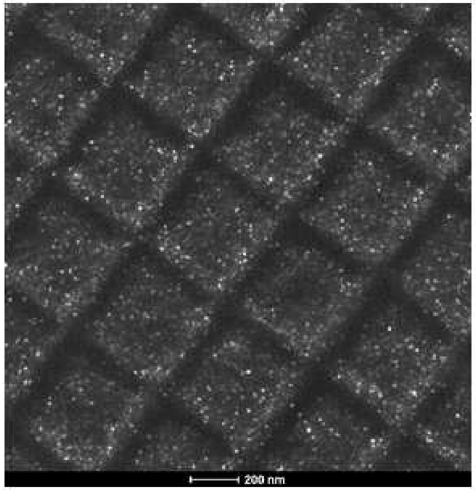
Note: samples in SEM are covered with thin layer of Pt or Au to avoid charging.

Methods of polymer morphology.

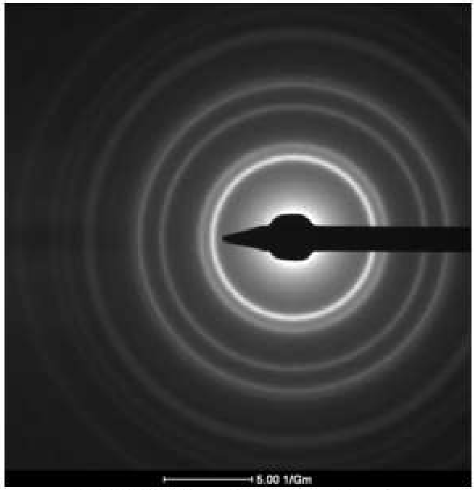
TEM = transmission electron microscopy: the most common modes.



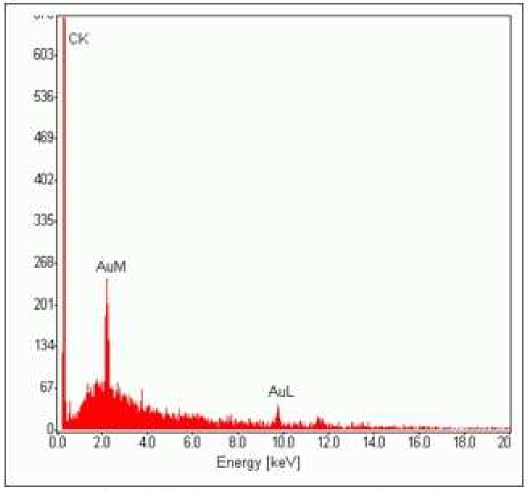
TEM/BF: Au standard
dark Au particles on light C film



TEM/DF: Au standard
white Au particles on dark C film



TEM/ED: Au standard
electron diffraction of Au on C



TEM/EDS: Au_standard
elemental analysis of Au on C

TEM/BF = bright field
detection of transmitted electrons
absorption + diffraction contrast
(heavier are elements darker)

TEM/DF = dark field
detection of diffracted electrons
diffraction contrast
(selected diffracting parts lighter)

TEM/ED = electron diffraction
detection of diffraction pattern
diffraction contrast
(nanocrystals give rings or spots)

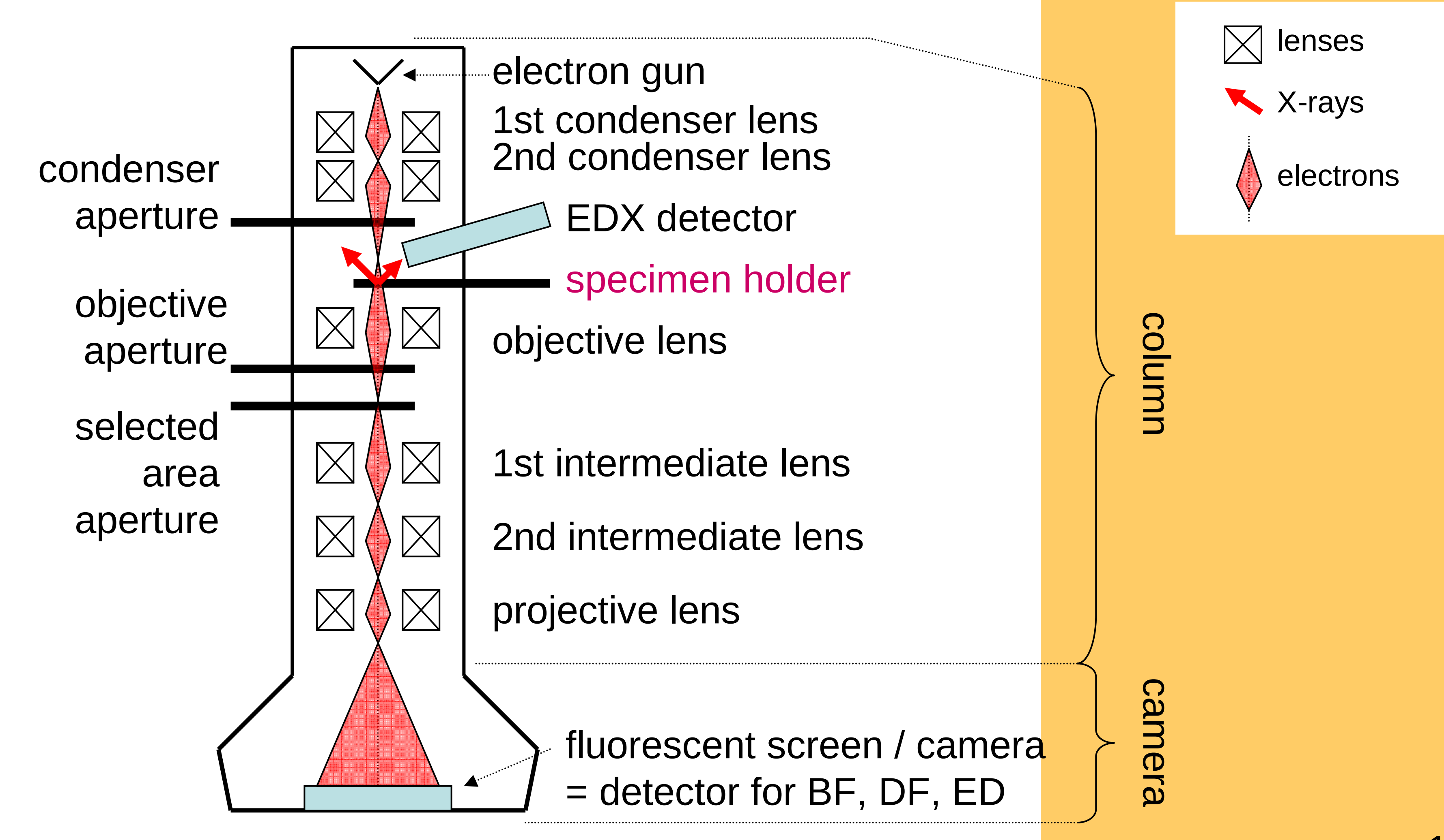
TEM/EDX = energy-dispersive
analysis of X-rays
(elemental analysis)
(analogy with SEM/EDX)

Methods of polymer morphology.

TEM: simplified scheme of microscope.

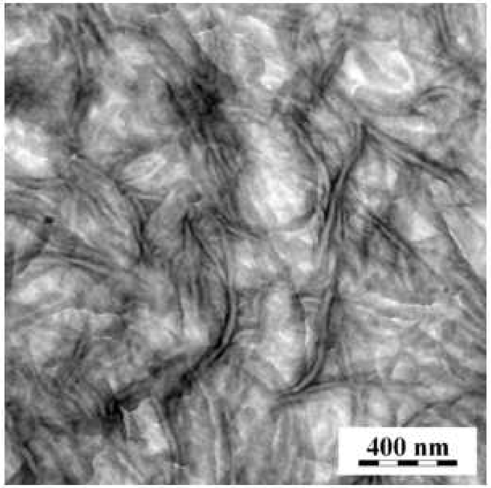
More details end of lecture

Schematic view of a standard TEM microscope

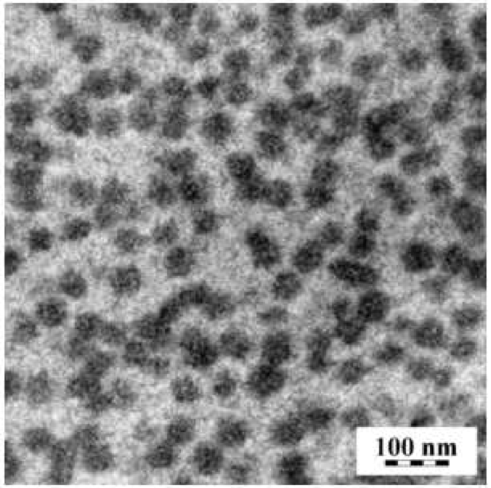


Methods of polymer morphology.

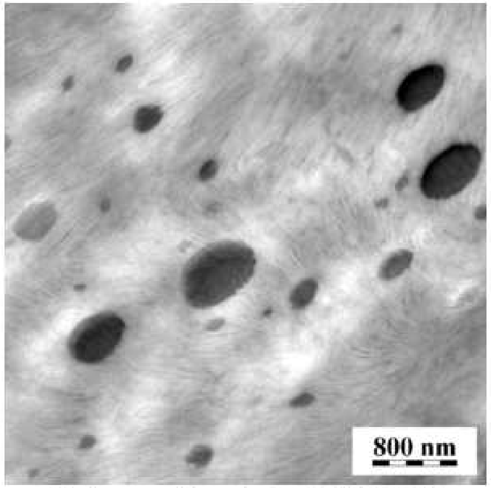
TEM: typical applications in polymer morphology.



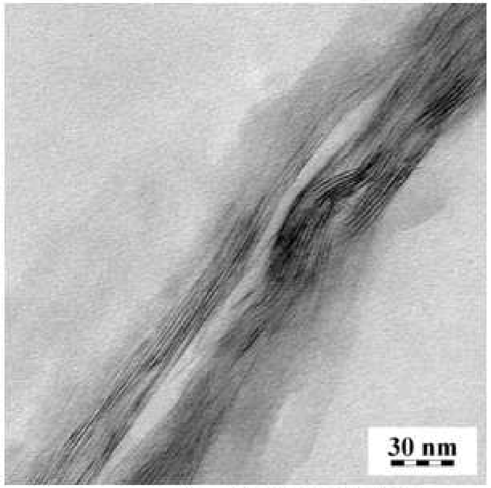
Homopolymer UHMWPE
semicrystalline structure



Copolymer based on PS
microphase separation of blocks



Polymer blend COC/LLDPE
(40/60), inverted structure



Composite PP/PA6/MMT
nanostructure of organoclay

TEM & polymer morphology.

Typical mode of TEM = TEM/BF:
probably >90% of applications

Typical specimens for TEM:
semicrystalline homopolymers
block copolymers
polymer blends
polymer nanocomposites
...

Typical sample preparation:
ultramicrotomy
= preparation of ultrathin (50nm) sections with ultramicrotome, a cutting device with diamond or freshly-broken-glass knives
* note: thickness of blade for shaving 100μm = 2000x more

Methods of polymer morphology.

Other methods: SPM/AFM, scattering methods, thermal methods, rheology...

Typical methods = what we have already shown ⇒ light and electron microscopy:

LM = light microscopy: transmitted × reflected × polarized light
SEM = scanning electron microscopy: SEM/SE, SEM/BSE, SEM/STEM, SEM/EDX
TEM = transmission electron microscopy: TEM/BF, TEM/DF, TEM/ED, TEM/EDX

Other methods, which yield information about polymer morphology:

SPM = scanning probe microscopy: AFM (atomic force), STM (scanning tunneling)...
diffraction/scattering: SAXS, WAXS, SANS, WANS, LS, DLS, QELS...
thermal methods: DSC, TGA
rheological measurements & DMA measurements

Note1: spectroscopic methods (like IR, UV/vis, NMR, ESR...) are focused mostly on molecular structure, not so much on supermolecular structure and morphology.

Note2: some of the methods will be presented in the following lectures.

Polymer structures.

(Incomplete) summary of typical polymer structures and morphologies.

Synthetic polymers

liquid state (mostly molecular level, mostly discussed in previous lecture)

molecules, agglomerates, micelles, micro/nanoparticles in solution

scattering methods (LS, QELS, SAXS, SANS), theoretical calculations...

solid state (mostly bulk materials, mostly discussed in this lecture)

homopolymers

amorphous: fracture surfaces, fracture lines (LM,SEM)

semicrystalline: structure of spherulites, lamellae (PLM,SEM,TEM,SWAXS)

polymer crystals: morphology (LM,TEM), crystal structure (TEM/ED)

copolymers

block copolymers: various morphologies (TEM, SAXS, AFM)

copolymers as compatibilizers: structure of compatibilized blends (SEM,TEM)

polymer blends

type of morphology (particulate, continuous...), compatibilization (SEM,TEM)

morphology-properties relationships: (SEM, rheology, mechanical testing...)

polymer composites

dispersion of filler in microcomposites (SEM) and nanocomposites (TEM)

morphology-properties relationships: (SEM, TEM, rheology, mech.testing...)

special cases

liquid crystalline polymers (PLM), hydrogels (LVSEM,ESEM), nanoparticles...

Polymer structures.

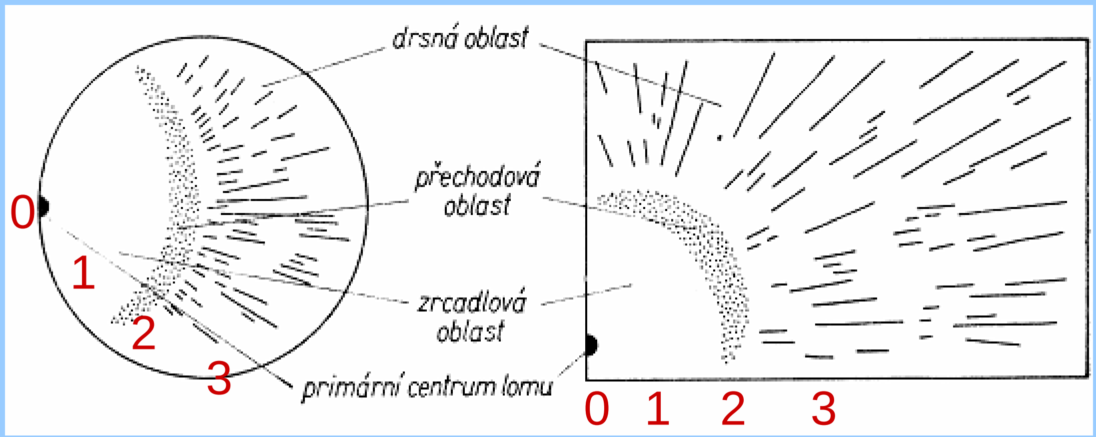
Amorphous polymers - brittle fracture surfaces.

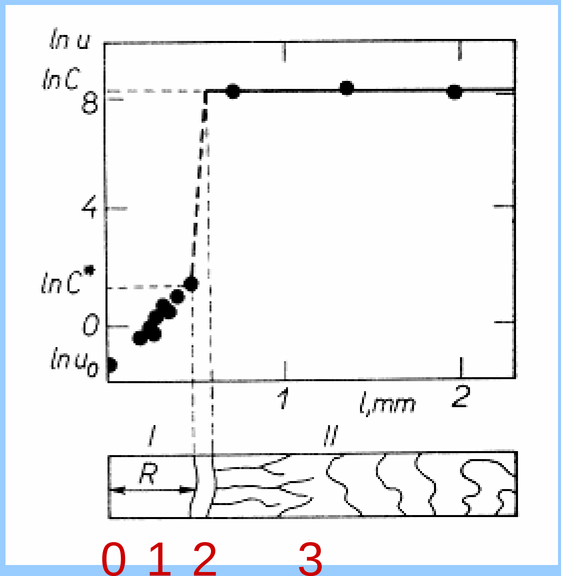
Structure of amorphous polymers is, at supermolecular level, homogeneous.

⇒ in a microscope we see no internal structure

⇒ but we can study deformation and fracture of homogeneous matrix

Brittle fracture of amorphous polymers (overall look of fracture surface)





Morphological features on fracture surfaces

(0) primary centre of fracture

(1) smooth region

(2) intermediate region (semi-rough)

(3) rough region (with conic markings - see next)

Speed of fracture propagation u as a function of distance l from primary centre of fracture

Connection with real life: fracture frequently starts at impurities/inhomogeneities.

Polymer structures.

Amorphous polymers - brittle fracture: crack, craze, fracture lines.

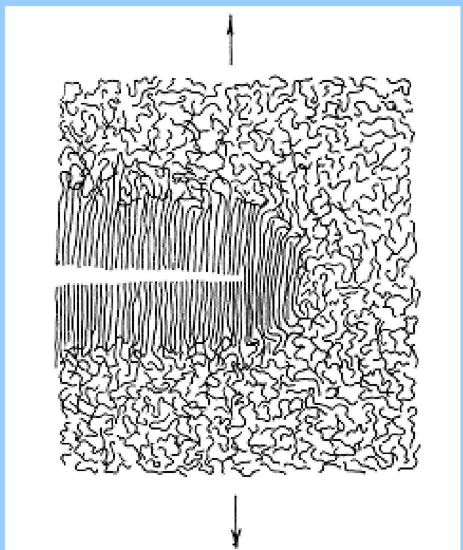
Propagation of fracture through polymers

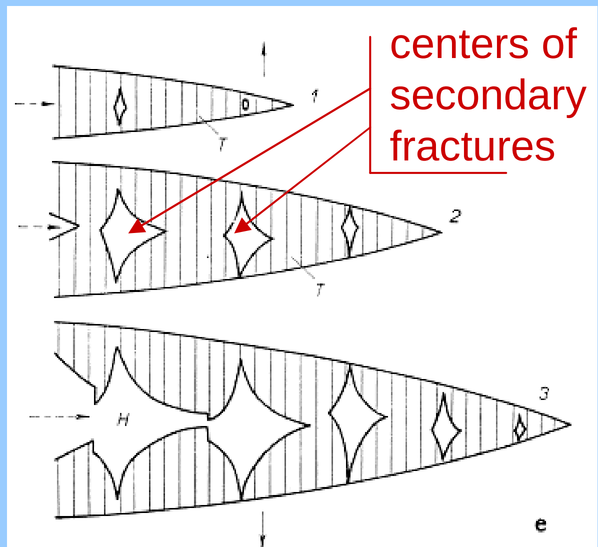
transformed region, oriented molecules, craze

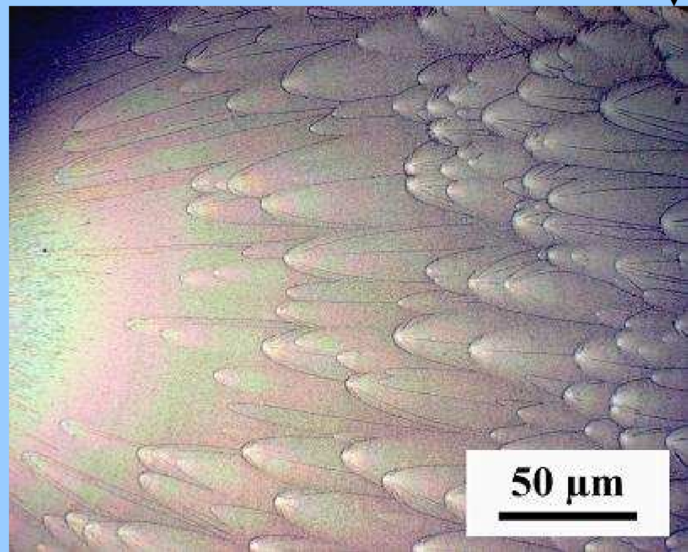
LM transmission

Crack → Craze →

LM reflection







Crack and craze at molecular level.

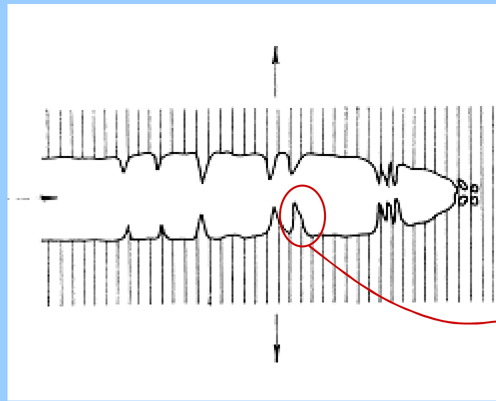
Combination of primary fracture and secondary fractures gives characteristic fracture markings/lines - usually conics.

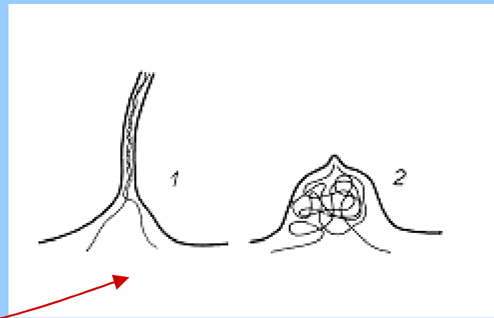
Polymer structures.

Amorphous polymers & other systems: brittle fracture × plastic deformations.

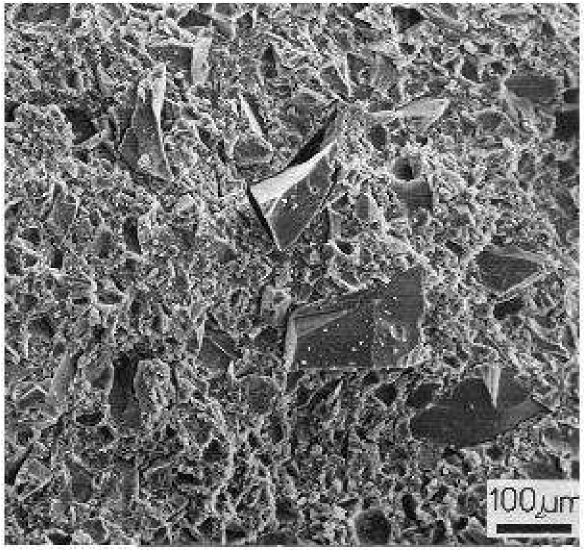
Types of fracture

- brittle fracture
  - ⇒ sharp fracture lines
- mixed fracture
  - ⇒ plastic (micro)deformations
- ductile fracture
  - ⇒ plastic (macro)deformations

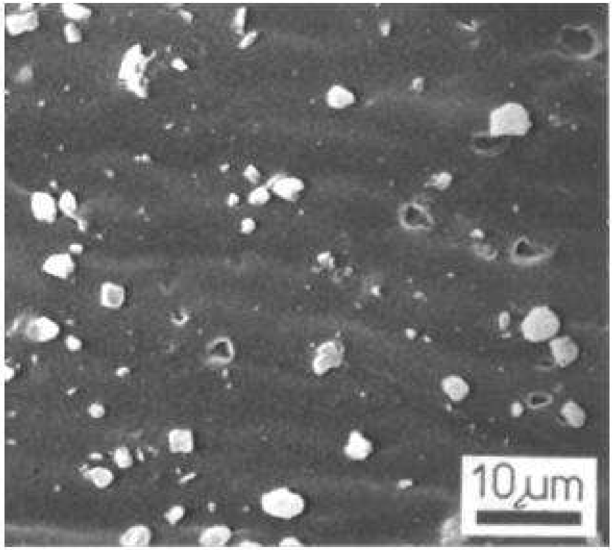




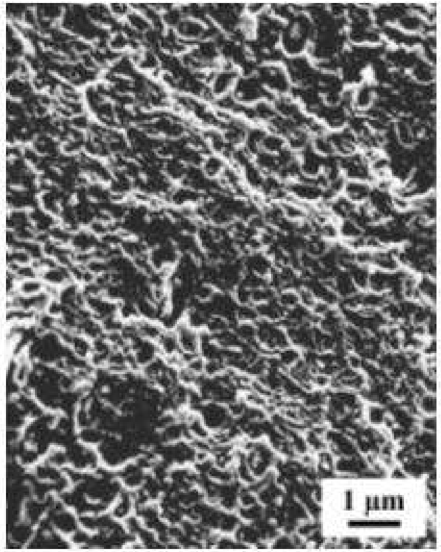
Plastic deformations at molecular level



Brittle fracture in a polymer composite



Ductile fracture in a polymer composite



Plastic deformations in ABS

SEM/SE micrographs showing brittle and ductile fracture in polymer systems.

Polymer structures.

Semicrystalline polymers - possible morphologies.

the fluid. Crystallization from an isotropic polymer fluid is usually incomplete with a sizable portion remaining uncrystallized. The more common morphologies observed include:

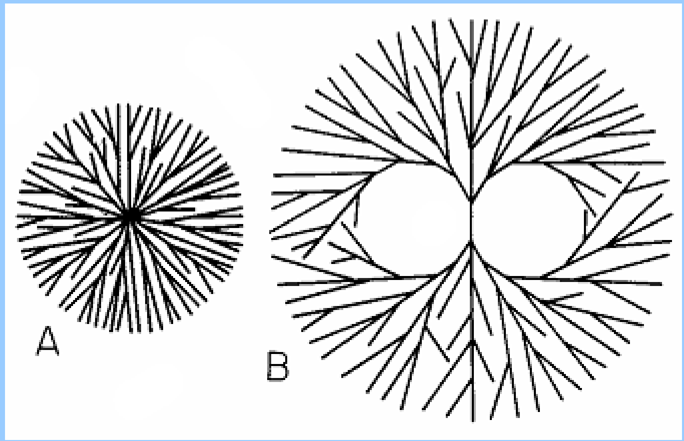
1. Faceted single lamellas containing folded or extended chains,
2. nonfaceted lamellas,
3. branched (dendritic) structures,
4. sheaf-like arrays of lamellar ribbons (axialites, hedrites),
5. spherulitic arrays of lamellar ribbons (spherulites),
6. fibrous structures, and
7. epitaxial lamellar overgrowths on microfibrils.

Other morphologies reported include aggregates of curved cup-shaped lamellas and crystallized gels. Further description of these various morphologies will be given below.

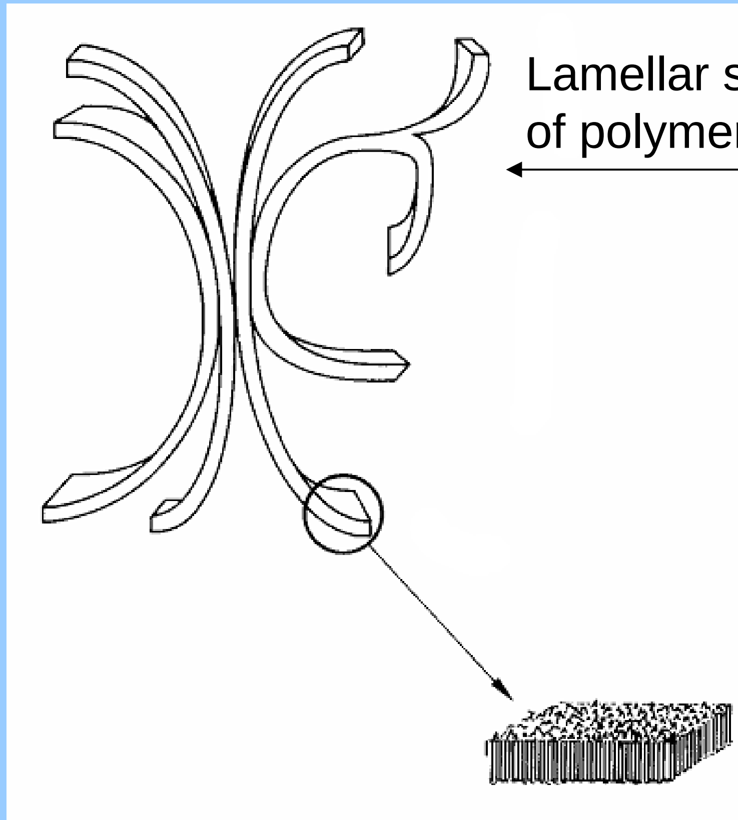
Semicrystalline polymers exhibit number of morphologies.
The most frequent are polymer spherulites.
The most important from for structure analysis are single lamellas.
Source: Woodward A E: Understanding polymer morphology.

Polymer structures.

Semicrystalline polymers - polymer spherulites (part1).

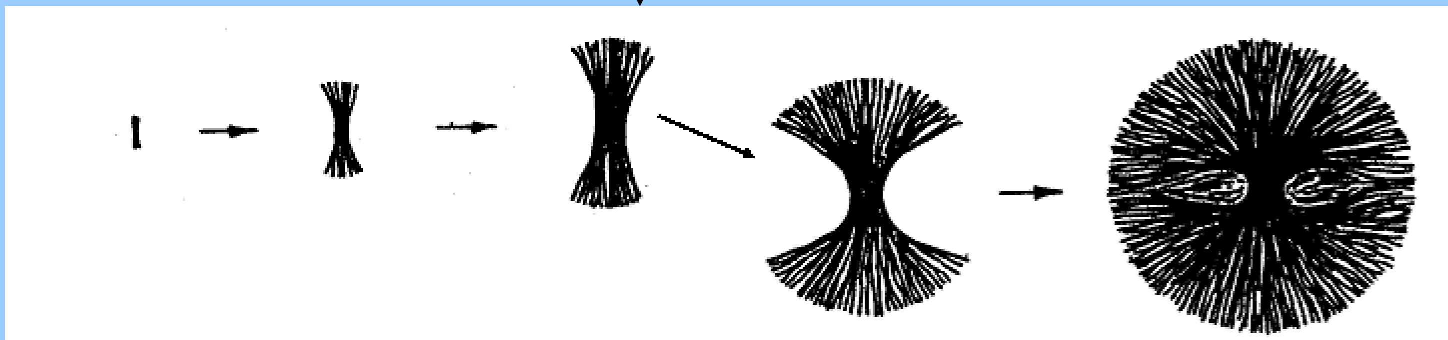


Growth of spherulites:
A) growth from center
B) lamellar bifurcation



Lamellar structure of polymer spherulites.

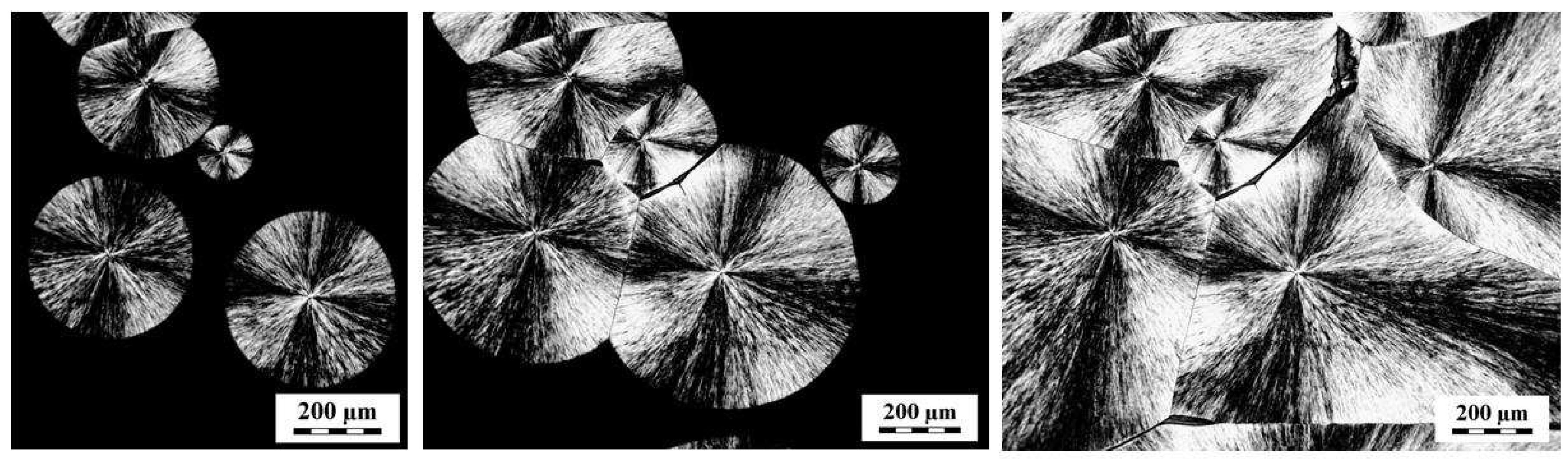
Growth of spherulites in time.



Polymer structures.

Semicrystalline polymers - polymer spherulites (part2).

Independent growth → Growing together → Completed crystallization

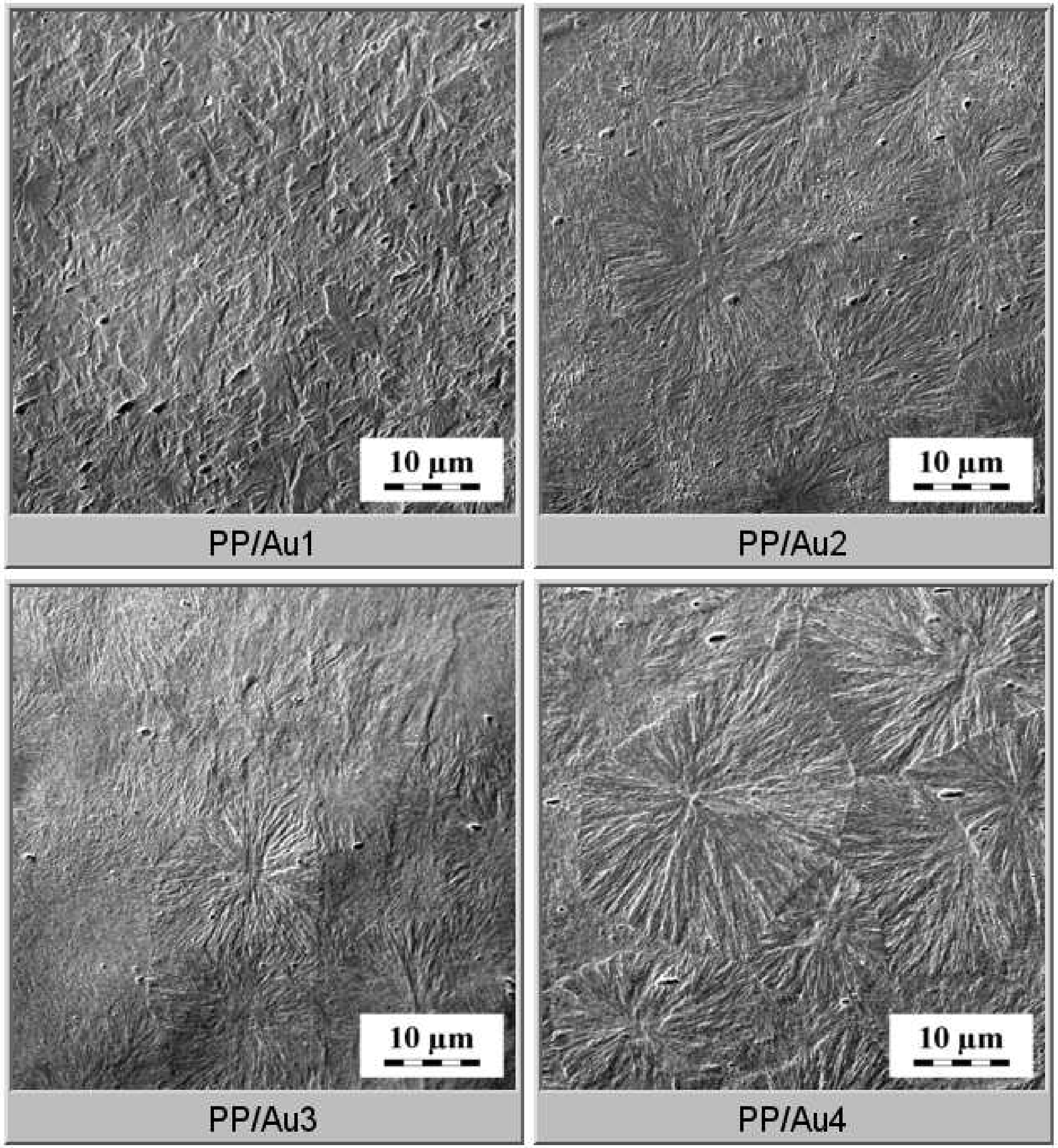


Spherulites of poly(ethylene oxide) = PEO.
Growth of spherulites is usually and easily observed
in polarized-light microscope equipped with a hot stage.

Note: in PLM the spherulites are usually grown between two microscopic glasses, which means that they are not spheres but very flat cylinders!
Real spherulites ARE spherical.

Polymer structures.

Semicrystalline polymers - polymer spherulites (part3).



Spherulites of polypropylene, which was nucleated by gold nanoparticles with various sizes (Au1 < Au2 < Au3 < Au4).

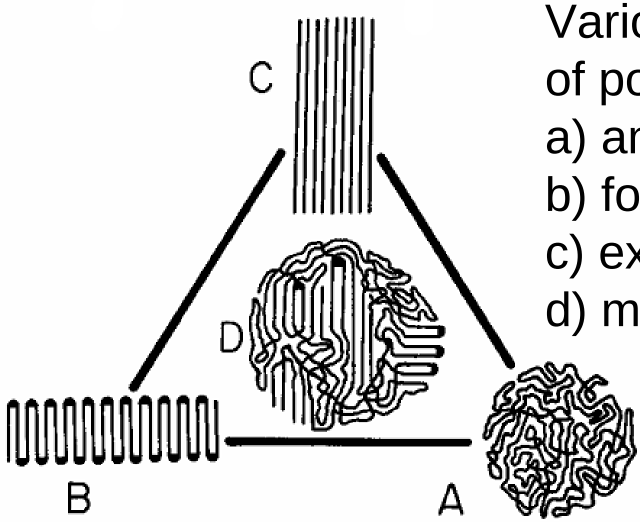
SEM/SE micrographs of cut surfaces etched by permanganic mixture. The mixture etches amorphous regions faster than crystalline lamellae.

Crystallization in bulk, i.e. in this case the spherulites are three-dimensional.

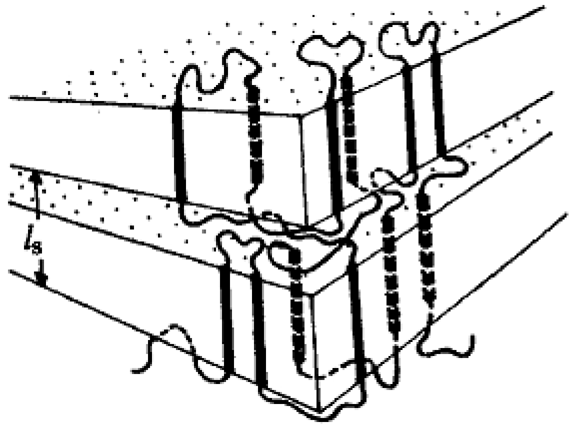
Source: IMC, group of polymer morphology.

Polymer structures.

Semicrystalline polymers - lamellas and amorphous regions (part1).

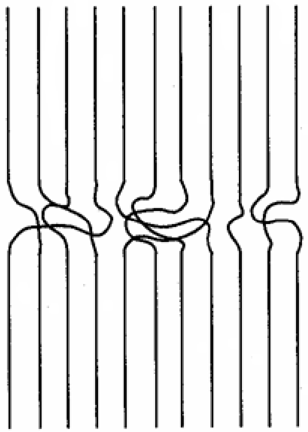


Various crystal forms of polymers:
a) amorphous
b) folded chains
c) extended chains
d) mixture of (a+b+c)

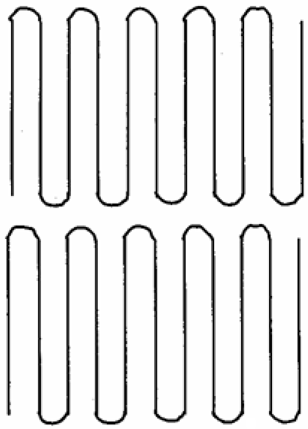


Crystalline lamellae and amorphous regions in 3D

Fringed micelles model



Random switchboard

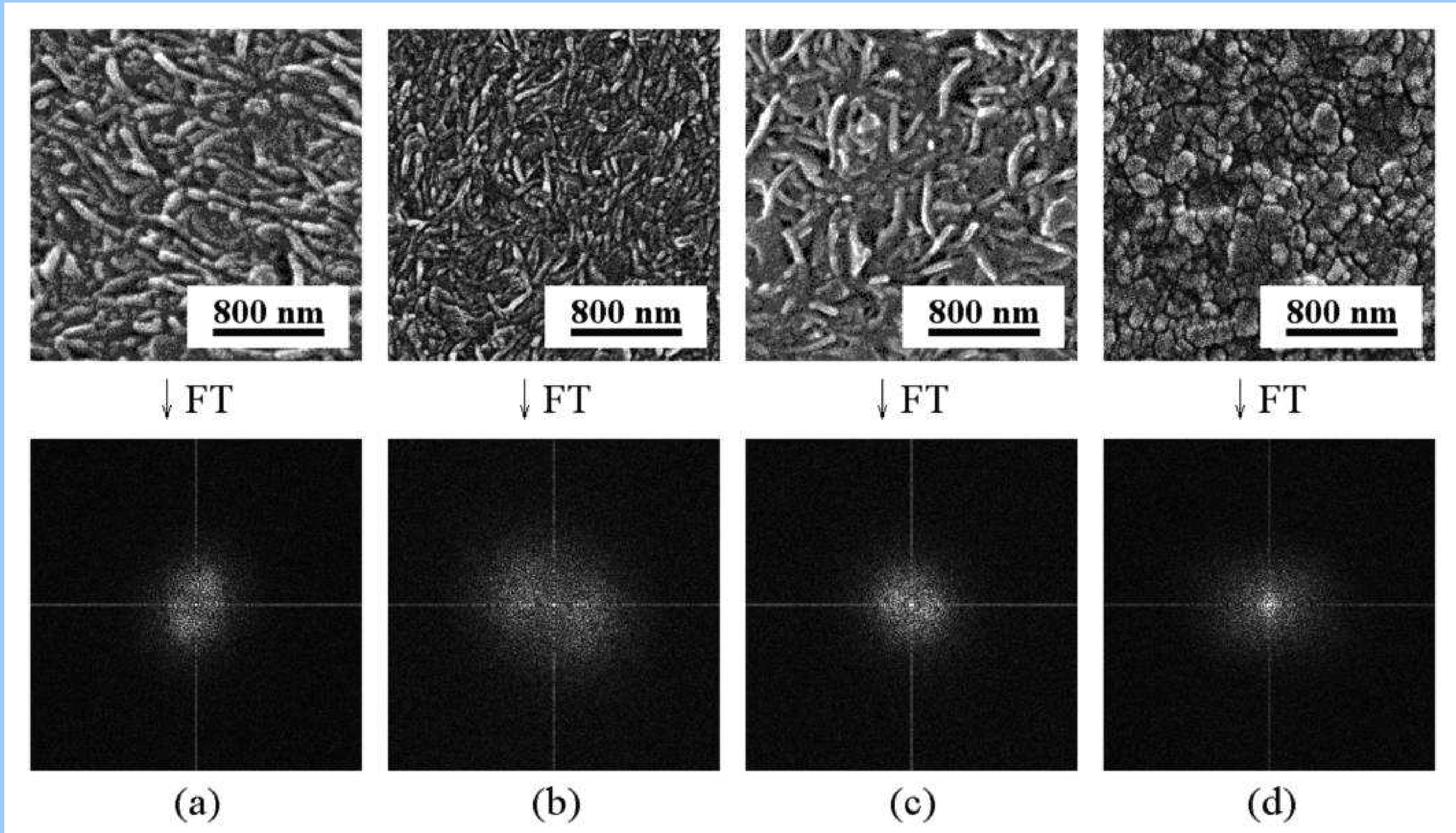


Folded chains crystals

Connection with real life: crystallinity influences mechanical properties, such as modulus and yield.

Polymer structures.

Semicrystalline polymers - lamellas and amorphous regions (part2).



UHMWPE is a semicrystalline polymer with non-spherulitic structure. Individual crystalline lamellae are visible after etching in SEM/SE at high magnifications. Source: Slouf M et al: *J.Biomed.Mater.Res.* 85B, (2008), 240.

Polymer structures.

Semicrystalline polymers - lamellas and amorphous regions (part3).

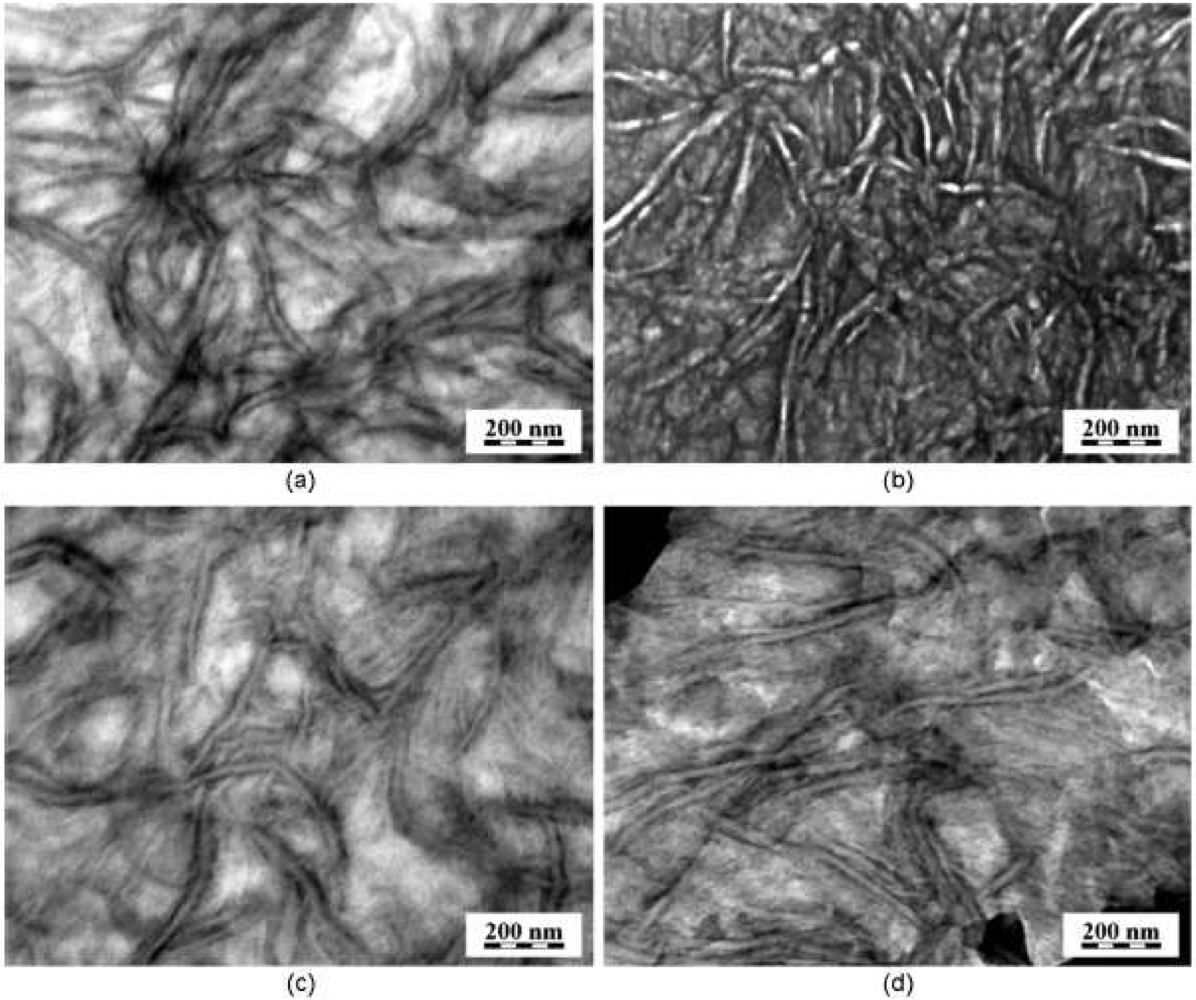


Figure 1. TEM micrographs showing the same UHMWPE sample (100 kGy_RM), which was stained in four different ways: (a) only HSO_3Cl, (b) $HSO_3Cl + (Ac)_2UO_2$, (c) only oleum, and (d) oleum + $(Ac)_2UO_2$. Detailed description of staining techniques is in the Experimental section.

Crystalline lamelae visualized at very high magnifications at TEM/BF.

Experimental:
1) ultramicrotomy
2) staining (4 ways)
3) TEM/BF

Source:
Stara H, Slouf M et al.
J. Macromol. Sci.- Phys, in press.

Polymer structures.

Polymer single crystals - morphology + crystal structure.

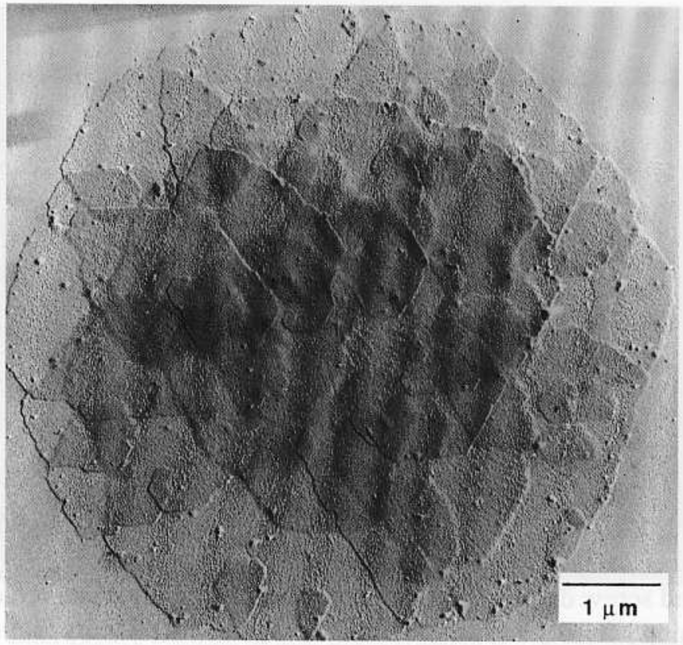


Figure 3.5 Transmission electron micrograph showing growth spirals on a polybutene-1 lamella crystallized from 0.01% pentyl acetate solution at 50 °C. [Reprinted with permission from: A.E. Woodward and D.R. Morrow, (1968) J. Polm. Sci. A-2 *6*, 1987. Copyright © 1968, John Wiley and Sons, Inc.]

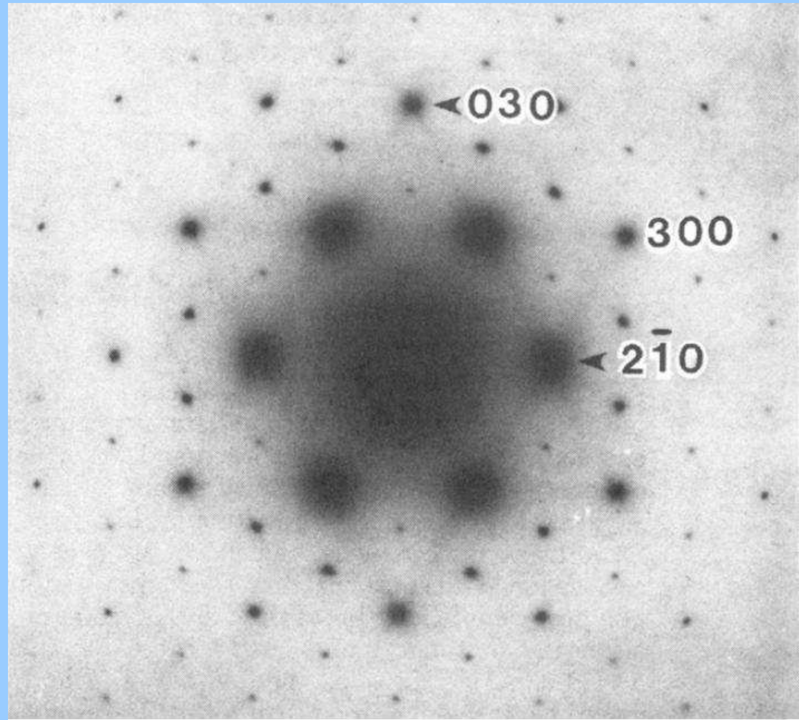


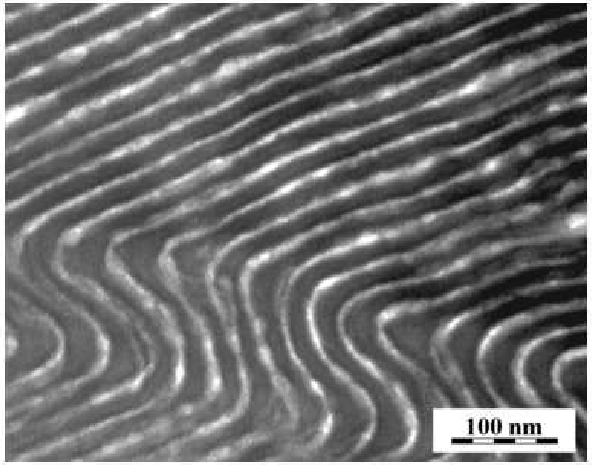
Figure 2. *hk*0 electron-diffraction pattern of β-iPP, hexagonal lamellae crystallized at 136 °C. The *b** axis is vertical (indexing with the trigonal A cell, Figure 1).

Polymer single crystals are slowly grown from diluted solutions.
Imperfections: loops, dislocations
Visualization: LM, TEM/BF, TEM/DF.

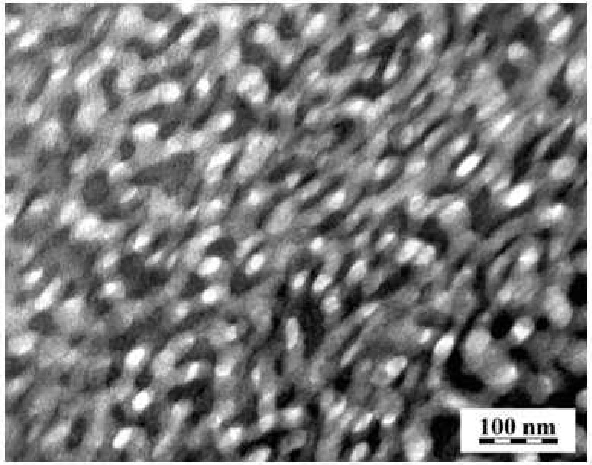
Structure of polymer single crystals is studied by TEM/ED.
Why not WAXS? ⇒ tiny dimensions and negligible scattering of X-rays.

Polymer structures.

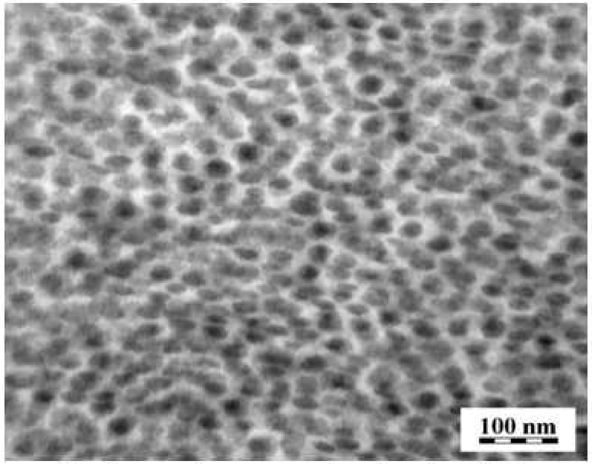
Copolymers: block copolymers - structure.



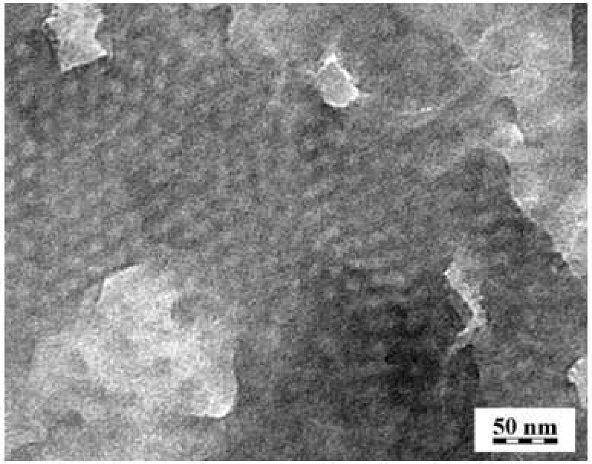
Block copolymer synthesized at IMC
lamellar structure



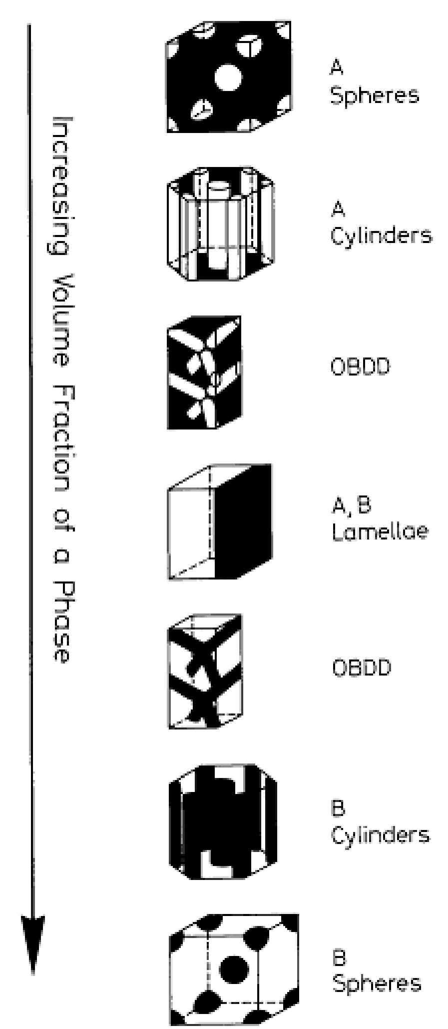
Block copolymer synthesized at IMC
irregular gyroid structure



Block copolymer synthesized at IMC
irregular cubic structure



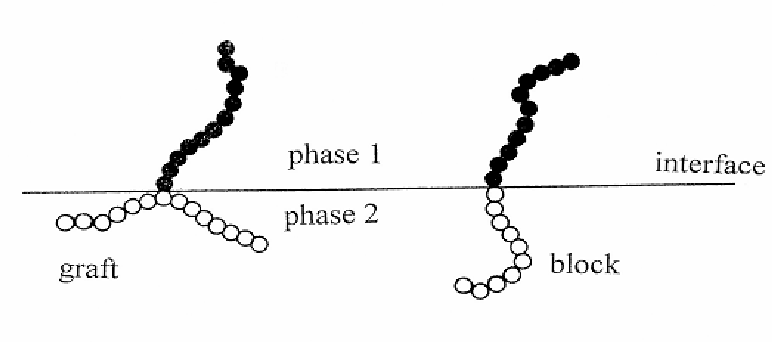
Block copolymer synthesized at IMC
hexagonal structure



Block copolymers $\rightarrow$ various morphologies $\rightarrow$ usually studied by TEM/BF.

Polymer structures.

Copolymers: block and grafted copolymers as compatibilizers.



Principle of compatibilization:

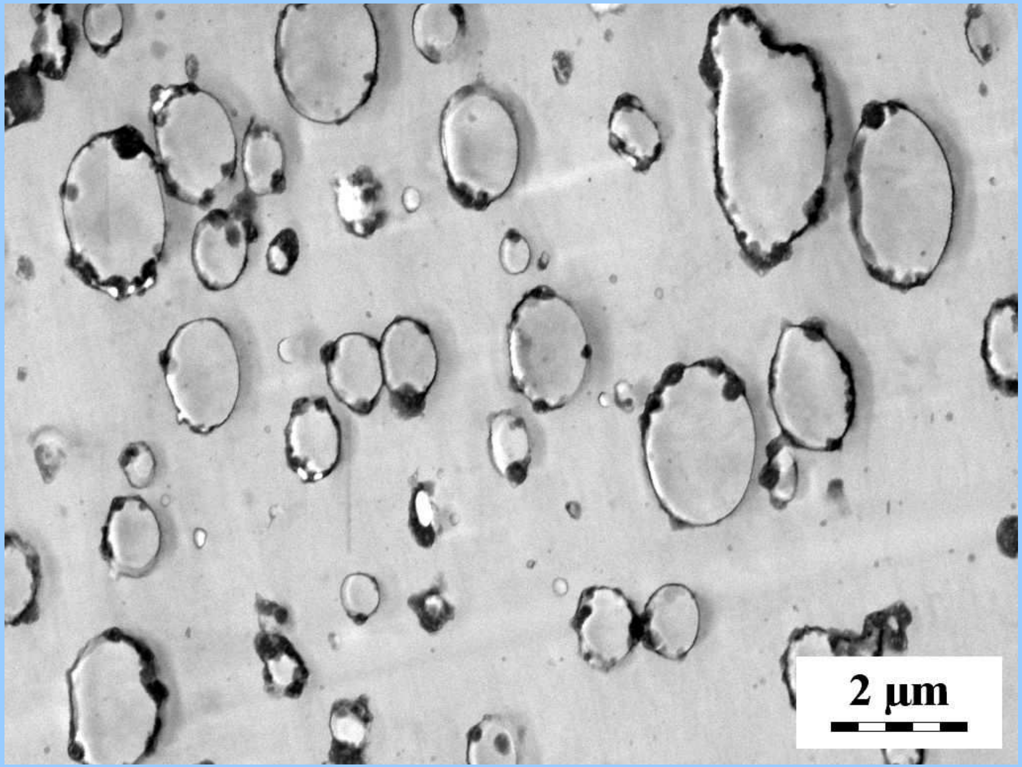
⇒ copolymer is localized at interface

⇒ stabilizes structure

⇒ limits coalescence (merging of particles)

⇒ why all this? big particles ⇒ bad properties

⇒ compatibilization is widely used in recycling...



SEM/STEM micrograph, polymer blend PS/LDPE/SB2 (80/20/5).

Experimental:

1) Ultramicrotomy.

2) Staining with OsO_4 vapors.

Source:

IMC, group of Polymer morphology.

Polymer structures.

Polymer blends - structures.

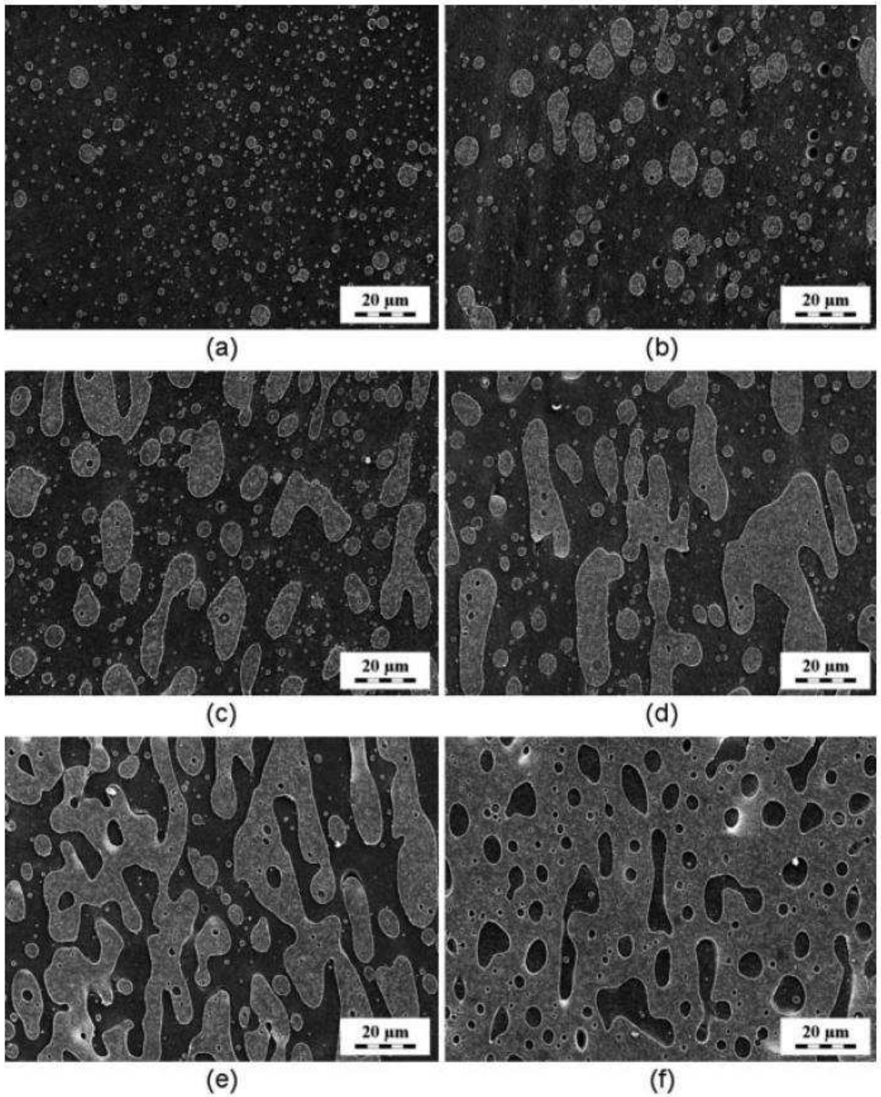
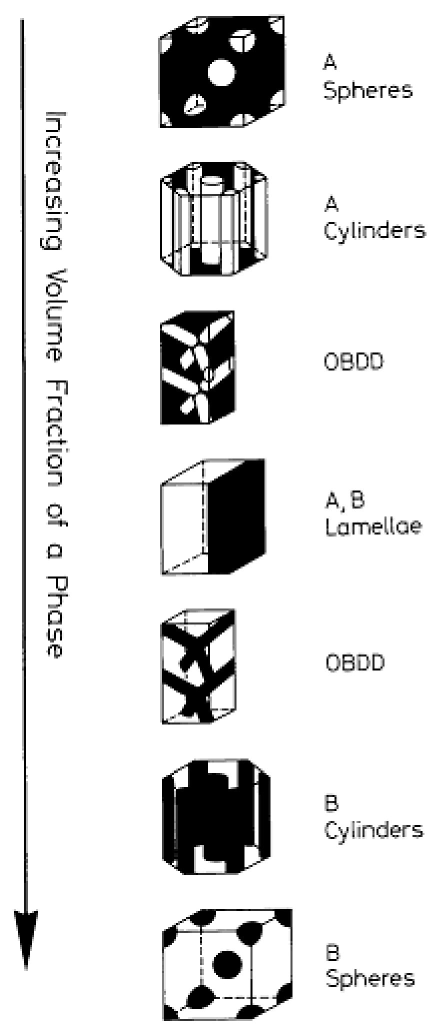


FIG. 5. SEM micrographs of noncompatibilized RTPP/ABS blends: (a) 90/10, (b) 80/20, (c) 70/30, (d) 60/40, (e) 50/50, and (f) 25/75.

Morphology (phase structure) of RTPP/ABS blends:
a) 90/10, b) 80/20, c) 70/30, d) 60/40, e) 50/50, f) 25/75.

Experimental:
1)smooth+etch
2)sputter with Pt
3)SEM/SE

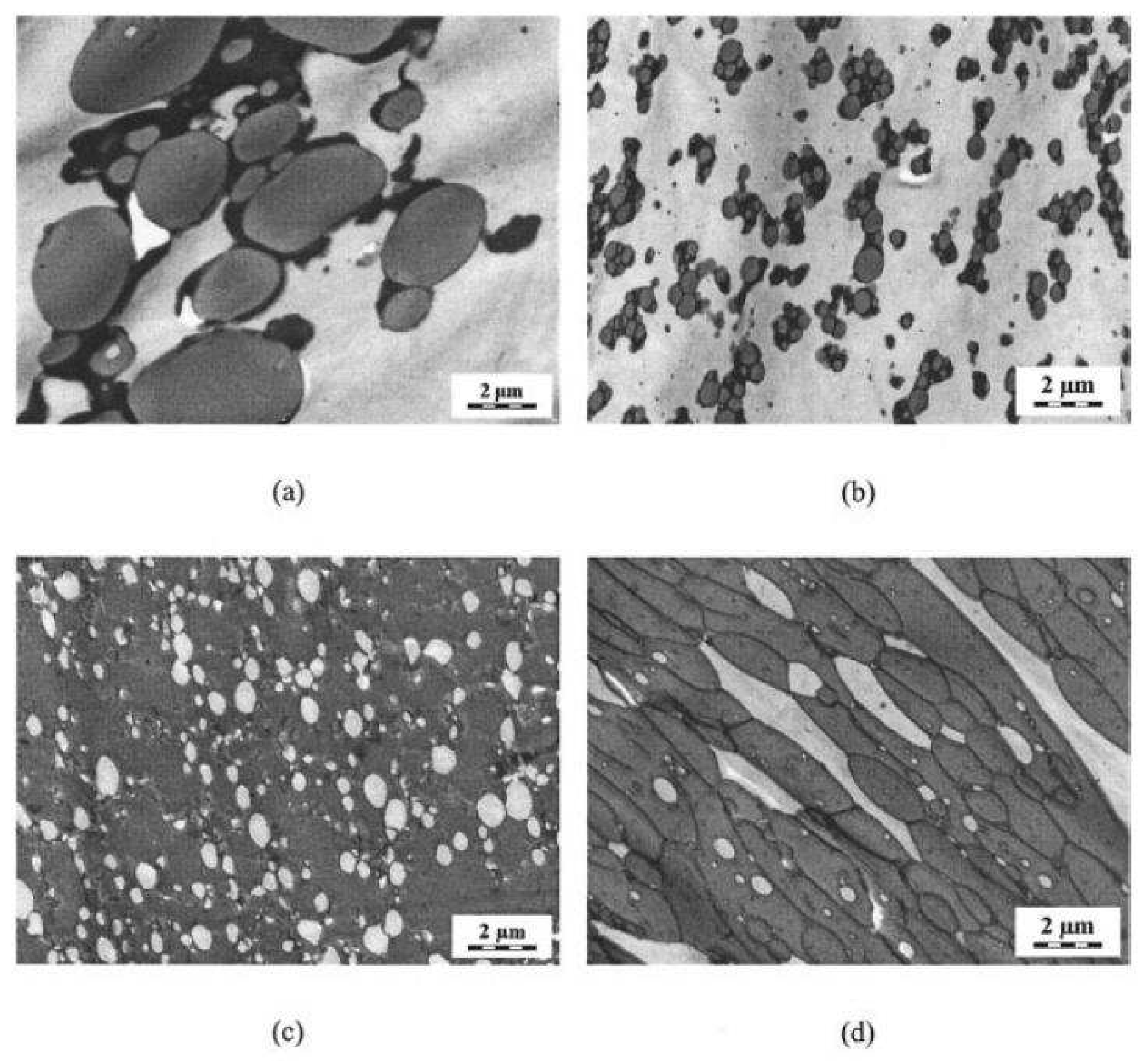
Note: structures of polymer blends are similar to those of block copolymers.



Source: Slouf M et al. *Polym. Eng. Sci.*, 47:582–592, 2007.

Polymer structures.

Polymer blends - compatibilization.



Source: Slouf M et al: *J Appl Polym Sci* 101: 2236–2249, 2006.

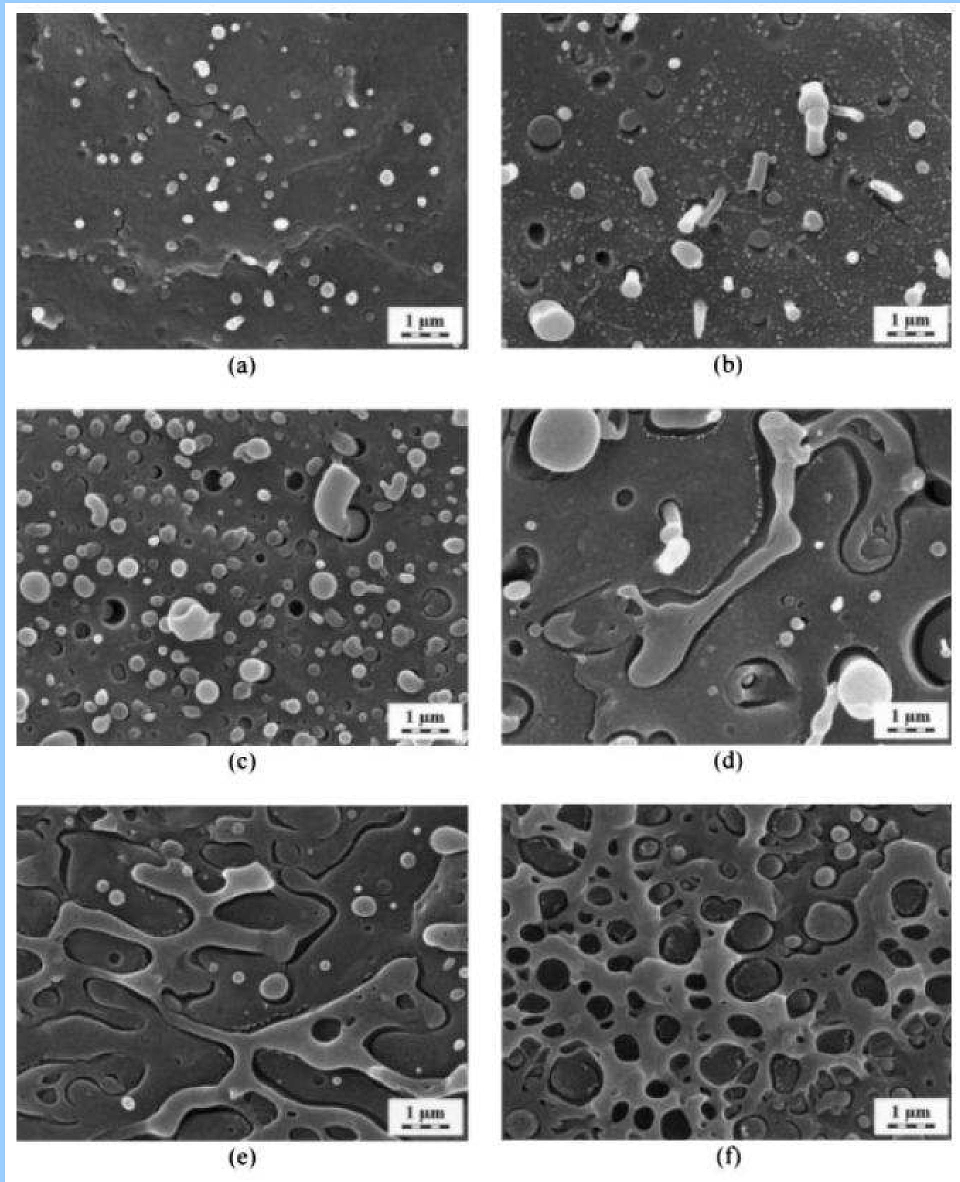
SEM/STEM micrographs of PP/PS/SEP blends:
a) 80/20/10, λ = 4
b) 80/20/10, λ = 0.4
c) 20/80/10, λ = 2.5
d) 20/80/10, λ = 0.25.
λ = ratio of torque moments
λ = TM(particles)/TM(matrix)

Experimental:
1) ultramicrotomy
2) RuO_4 staining
3) SEM/STEM
$\Rightarrow$ PP = white
PS = gray
SEP = black

Conclusions:
SEP is a good compatibilizer
morphology influenced by λ

Polymer structures.

Polymer blends - morphology & properties. (PP/COC, part1)



SEM/SE micrographs showing morphology of polymer blend PP/COC.
a) 90/10, b) 80/20, c) 70/30,
d) 60/40, e) 50/50, f) 25/75.
* PP = polypropylene
* COC = cycloolefin copolymer
(copolymer of ethylene and norbornene

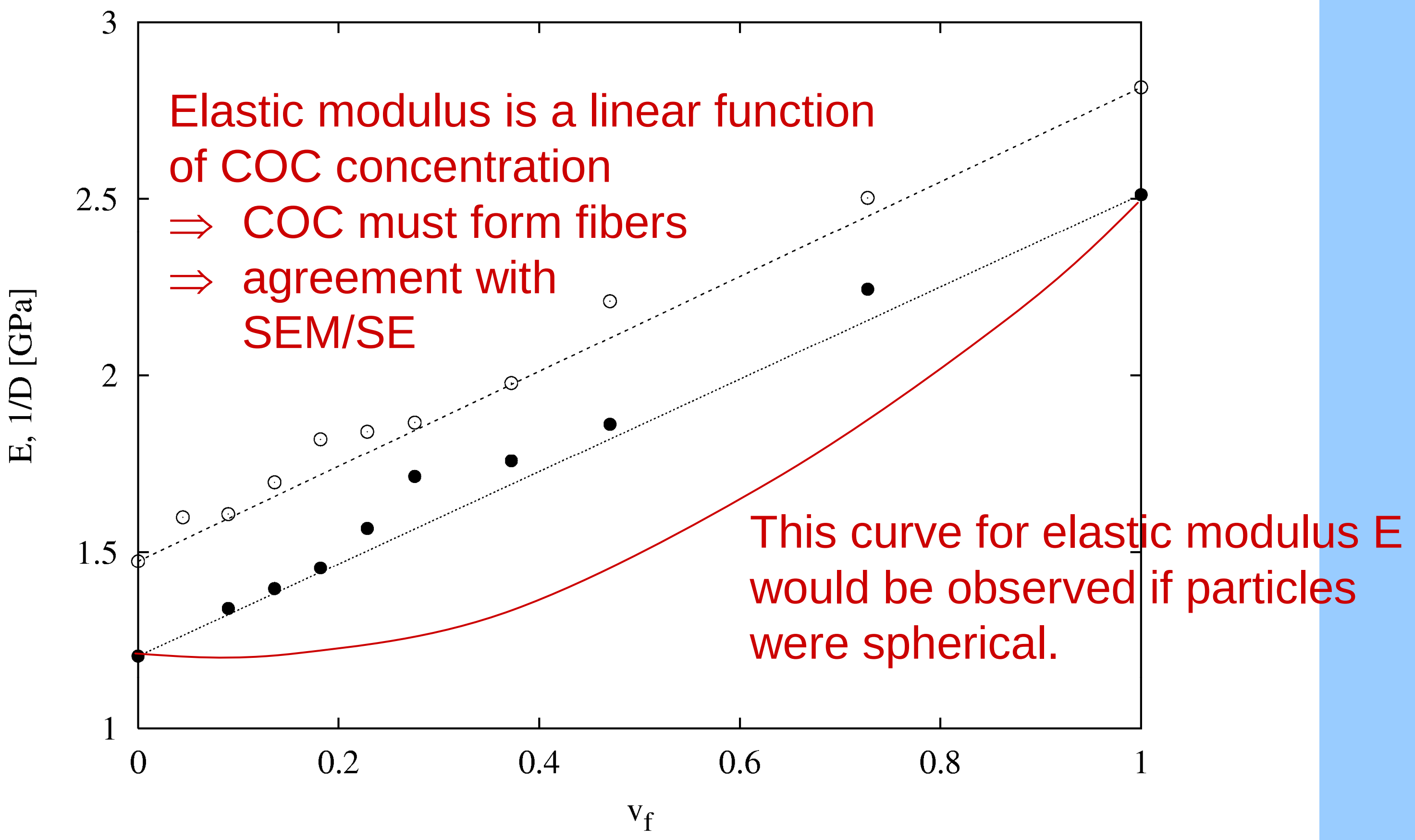
Experimental:
1) Fracture in LN_2 (liquid nitrogen).
(perpendicular to injection direction)
2) Sputter with 4nm-thick layer of Pt.
3) Observe in SEM/SE.

Note:
1) Fibrous morphology of COC.
2) Phase co-continuity at 60/40.
3) Phase inversion at 50/50.

Source: Slouf M et al:
J Appl Polym Sci 91: 253–259, 2004.

Polymer structures.

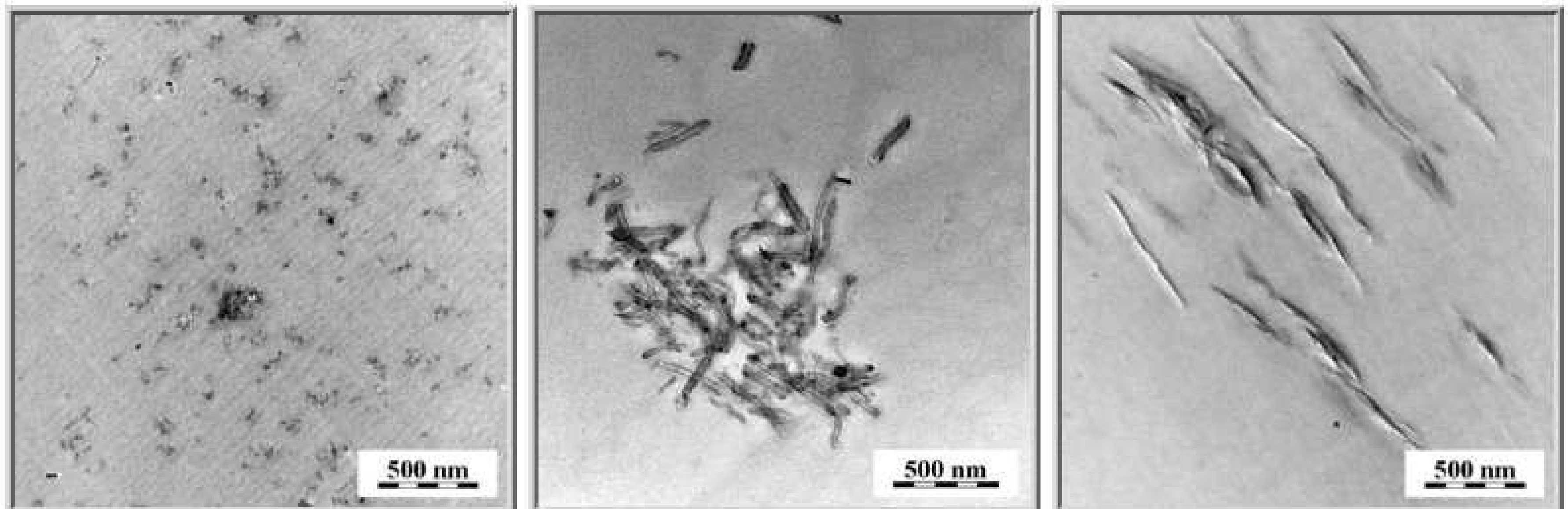
Polymer blends - morphology & properties. (PP/COC, part2)



Elastic modulus, E, and reciprocal compliance, 1/D, as a function of COC concentration, v_f.

Polymer structures.

Polymer composites - dispersion of filler.



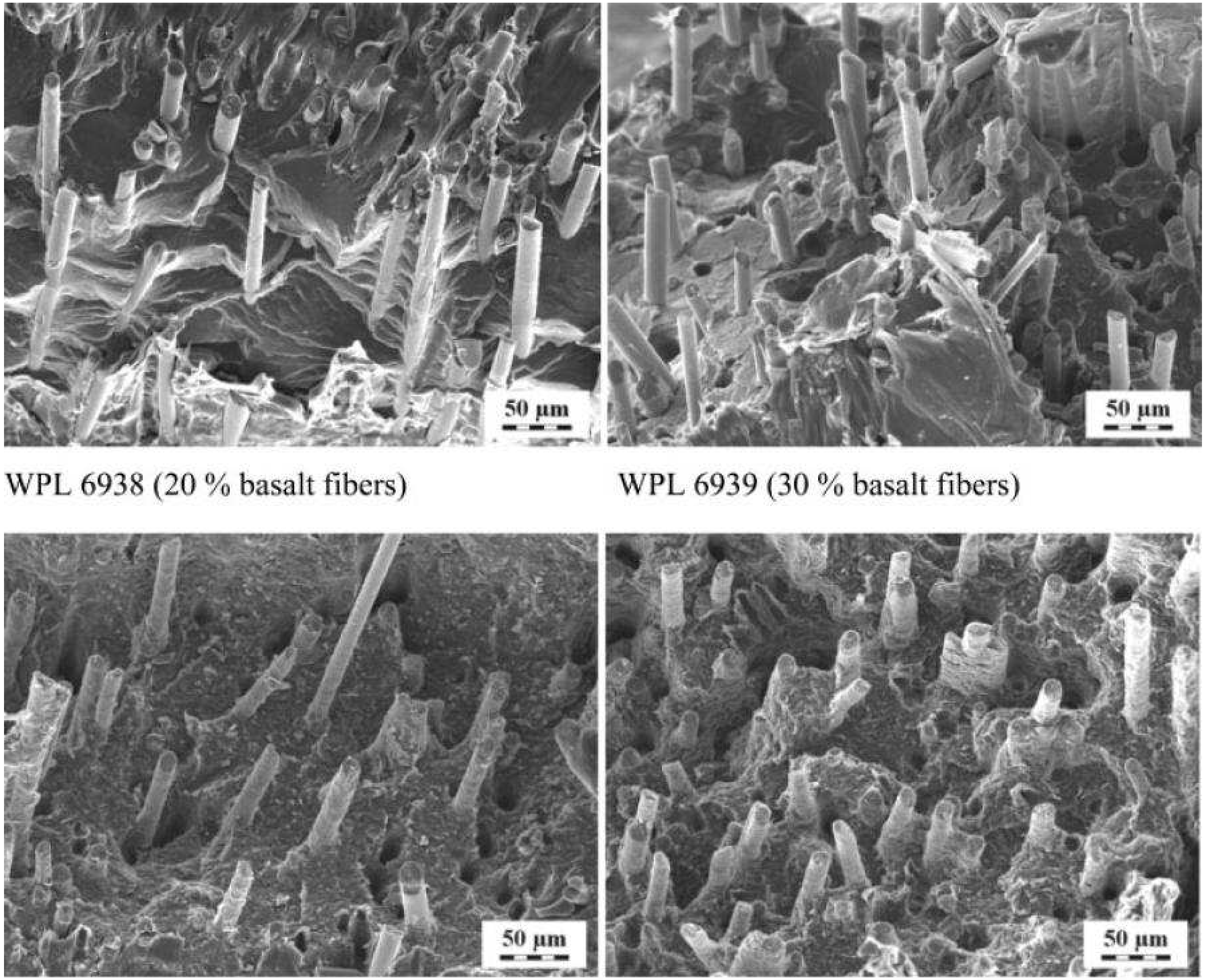
(a) PS/nanoCaCO3_5% (b) Epoxy/CNT_5% (c) PS/MMT_5%

TEM/BF micrographs of various polymer nanocomposites with
(a) 0D-nanoparticles = $CaCO_3$ nanopowder
(b) 1D-nanoparticles = carbon nanotubes
(c) 2D-nanoparticles = montmorilonite

Good dispersion of the filler in nanocomposites (and microcomposites) is very important, because it (almost always) holds: bad dispersion ⇒ bad properties.

Polymer structures.

Polymer composites - morphology & properties. (rPET/BF, part1)



WPL 6938 (20 % basalt fibers) WPL 6939 (30 % basalt fibers)

WPL 6941 (20 % basalt fibers, 10 % talc) WPL 6940 (30 % basalt fibers, 10 % talc)

SEM/SE micrographs of rPET/BF composites.
rPET = recycled PET
BF = basalt fibles

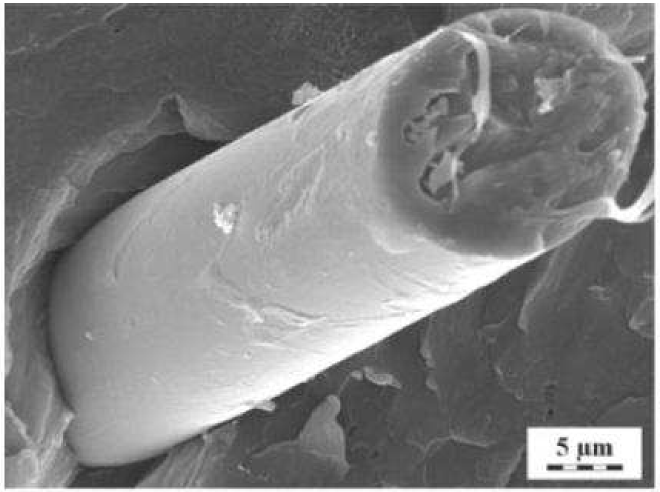
Experimental:
1)Fracture in LN_2.
2)Sputter with Pt.
3)SEM/SE.

Note:
higher interfacial adhesion in rPET/BF/talc.

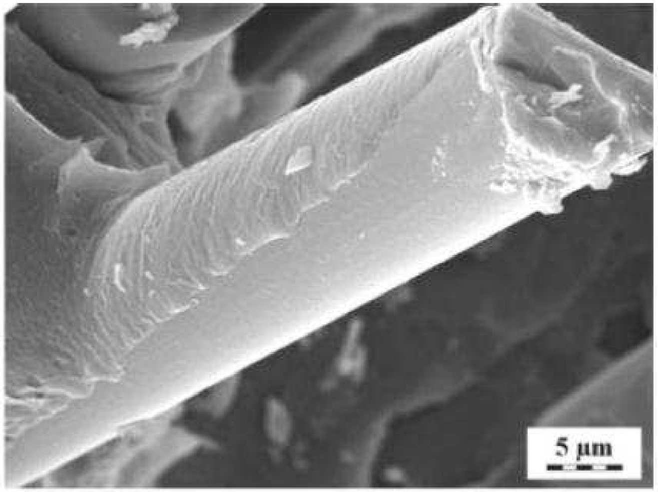
Source:
Kracalik M et al: Polym. Compos., 29:437–442, 2008.

Polymer structures.

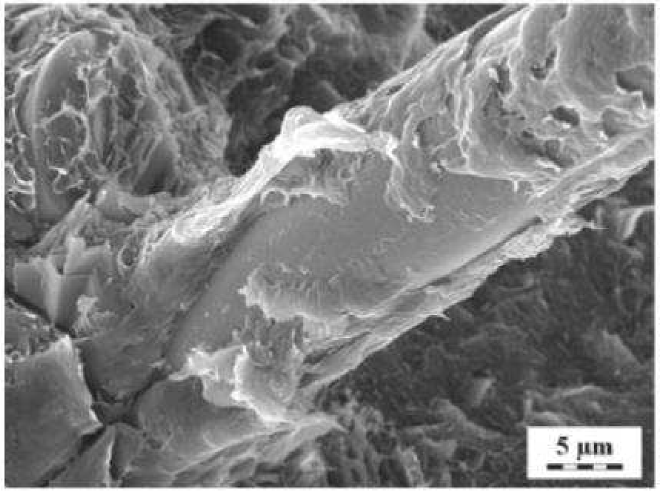
Polymer composites - morphology & properties. (rPET/BF, part2)



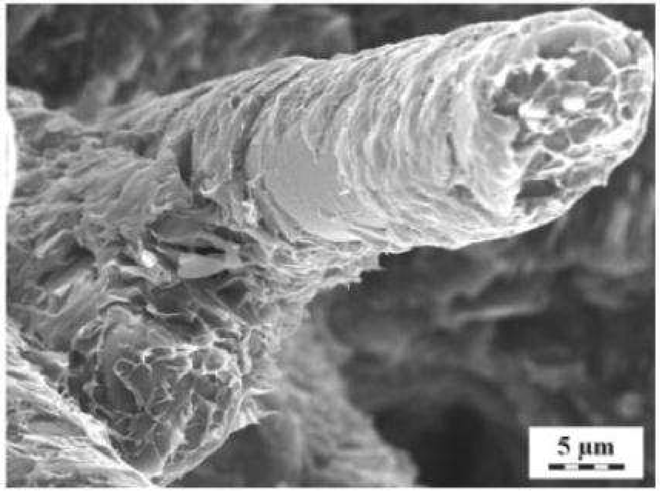
WPL 6938 (20 % basalt fibers)



WPL 6939 (30 % basalt fibers)



WPL 6941 (20 % basalt fibers, 10 % talc)



WPL 6940 (30 % basalt fibers, 10 % talc)

SEM/SE micrographs of single basalt fibers in rPET/BF composites.

Higher magnification micrographs demonstrate increased interfacial adhesion between rPET and BF in presence of talc.
$\Rightarrow$ in rPET/BF/talc composites,
BF are more covered with rPET.

Polymer structures.

Polymer composites - morphology & properties. (rPET/BF, part3)

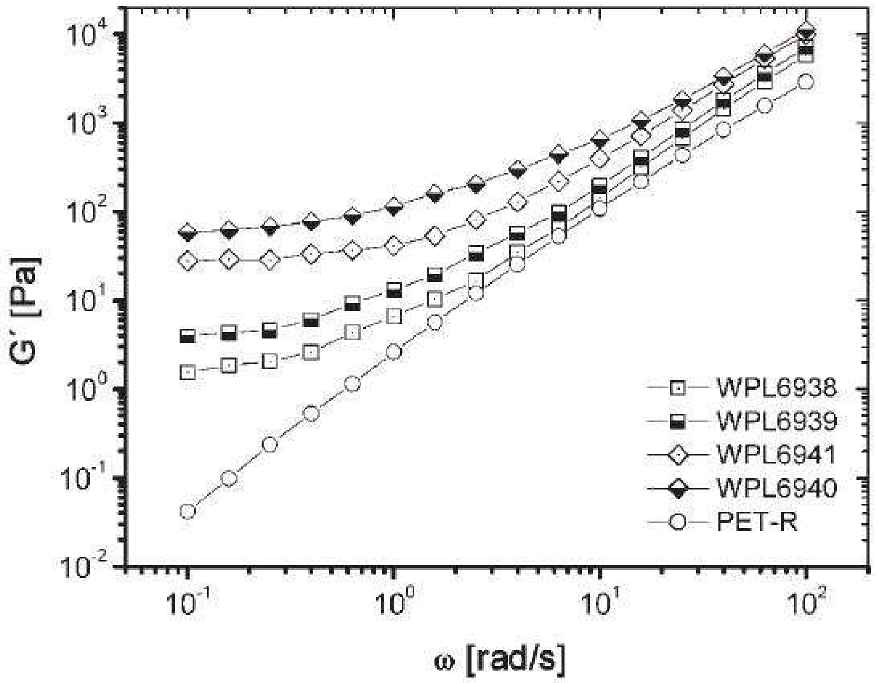


FIG. 4. Storage modulus of the matrix and composites.

TABLE 3. Mechanical properties of composites.

Properties	WPL 6938	WPL 6939	WPL 6941	WPL 6940
Tensile strength (MPa)	95	112.9	100.7	122.8
Elongation at break (%)	2.9	2.9	2.1	2.2
Tensile modulus (MPa)	6,418	8,655	9,693	12,770
Flexural modulus (MPa)	5,639	7,739	8,817	11,750
Impact strength (kJ/m^2)	32.2	43.5	40.9	41.7
Notch impact strength (kJ/m^2)	5.7	8.1	5.4	5.7

Rheological and mechanical properties of rPET/BF systems.
The highest elastic modulus exhibits composite with 30% of fibers and 10% of talc.
According to SEM/SE, this system has good dispersion and good interfacial adhesion.
⇒ good agreement between morphology and properties

Conclusion.

Take-home messages.

1) Polymer morphology deals with structure of polymer systems, mostly in solid state.

2) Polymer morphology is studied because of the strong relationship [morphology-properties].

3) Polymer morphology can give a lot of information, mostly about: homopolymers, copolymers, polymer blends, micro- and nanocomposites... (but also about polymer hydrogels, micelles, nanoparticles, liquid crystals...

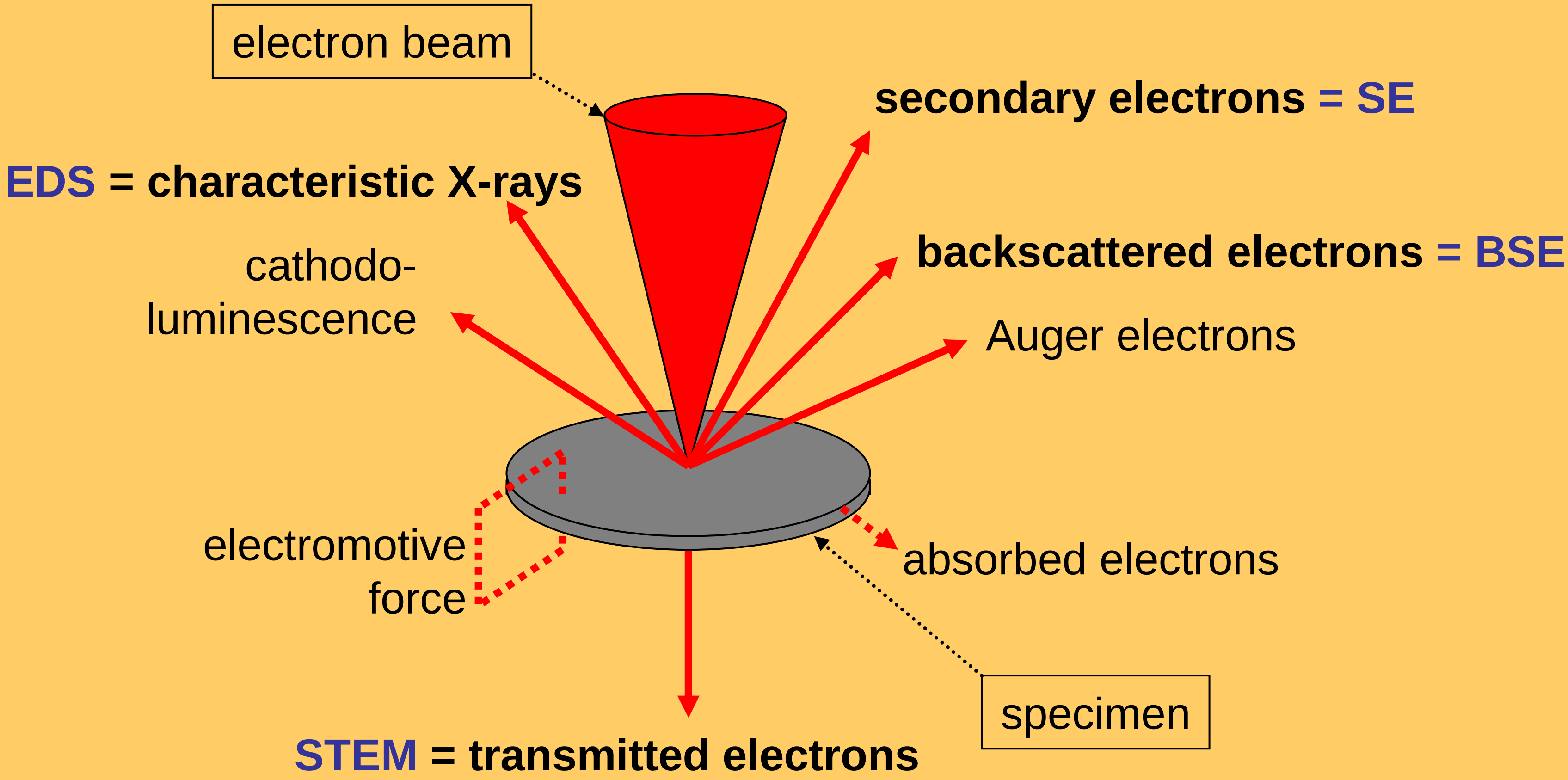
4) Polymer morphology at IMC is (to be modest) at quite high level. If you have a morphological problem - do not hesitate to contact us!

Final note: Thank you for your attention!

Methods of polymer morphology.

SEM: interaction of electrons and specimen.

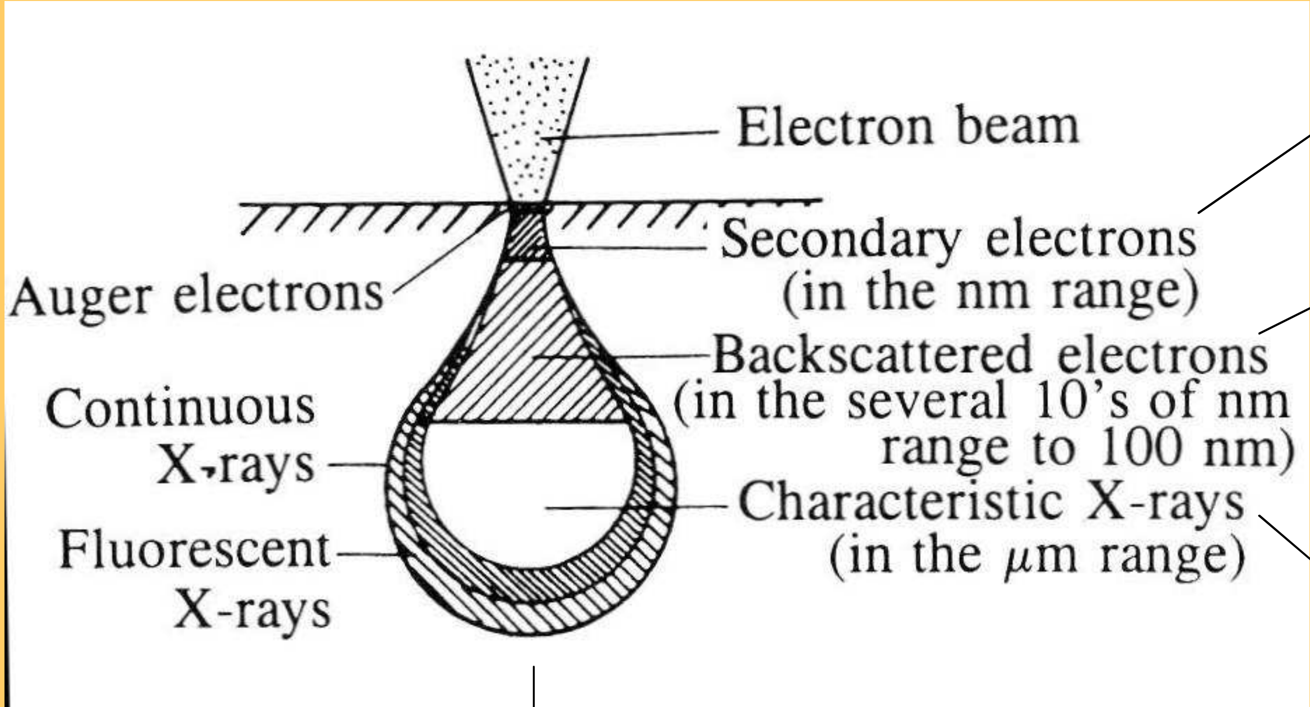
Interaction of electron beam with specimen - various signals in SEM



Methods of polymer morphology.

SEM: interaction of electrons with specimen × resolution.

Interaction of electron beam with specimen - resolutions in SEM



SE resolution
ca 1-10 nm

BSE resolution
ca 10-100 nm

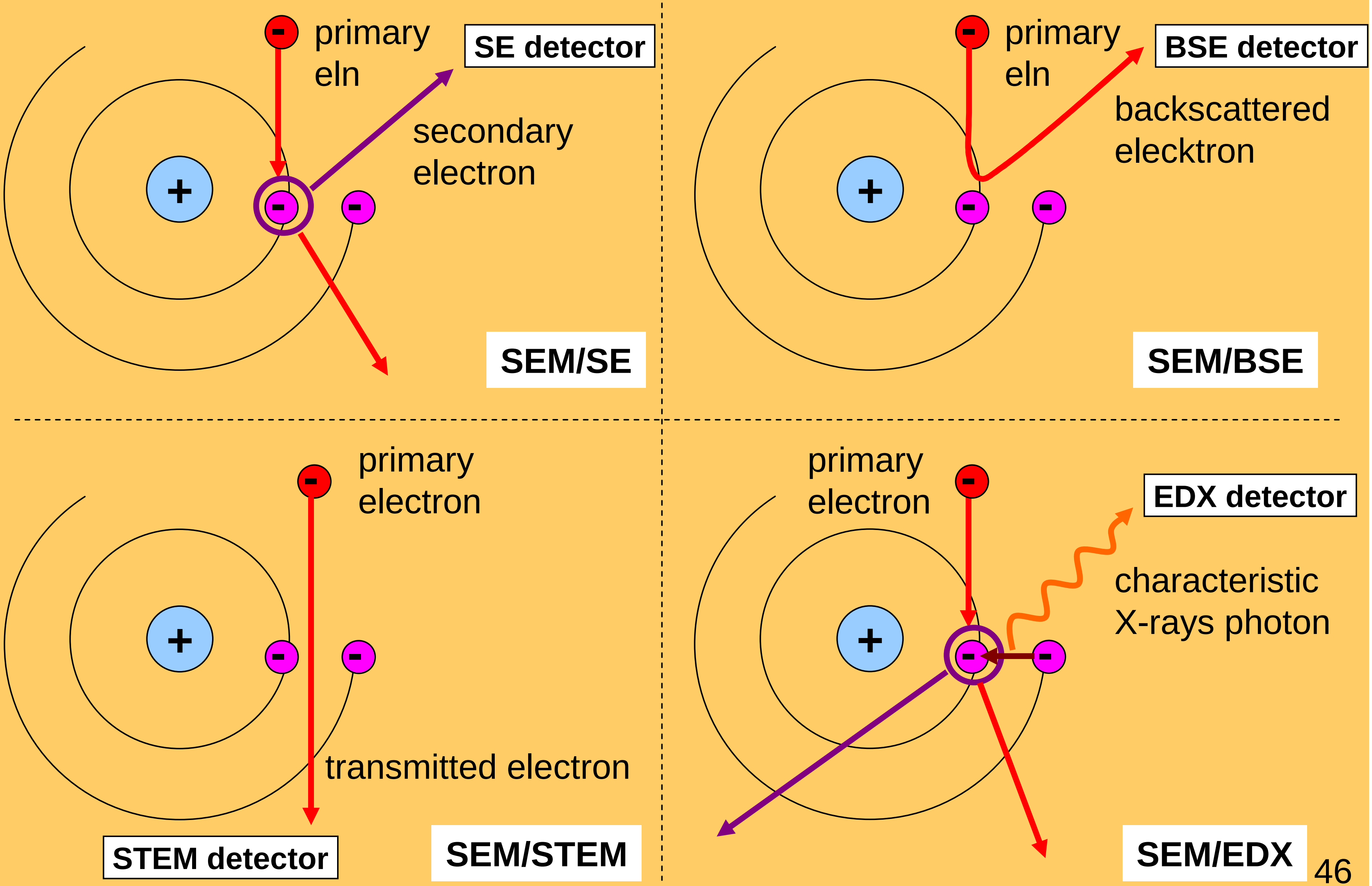
EDX resolution
ca 1-10 μm

STEM resolution depends on sample thickness,
usually it is comparable to that of SE, i.e. ca 1-10 nm.

Resolution in SEM is given by: (1) spot size, (2) mode, (3) HV, (4) specimen...

Methods of polymer morphology.

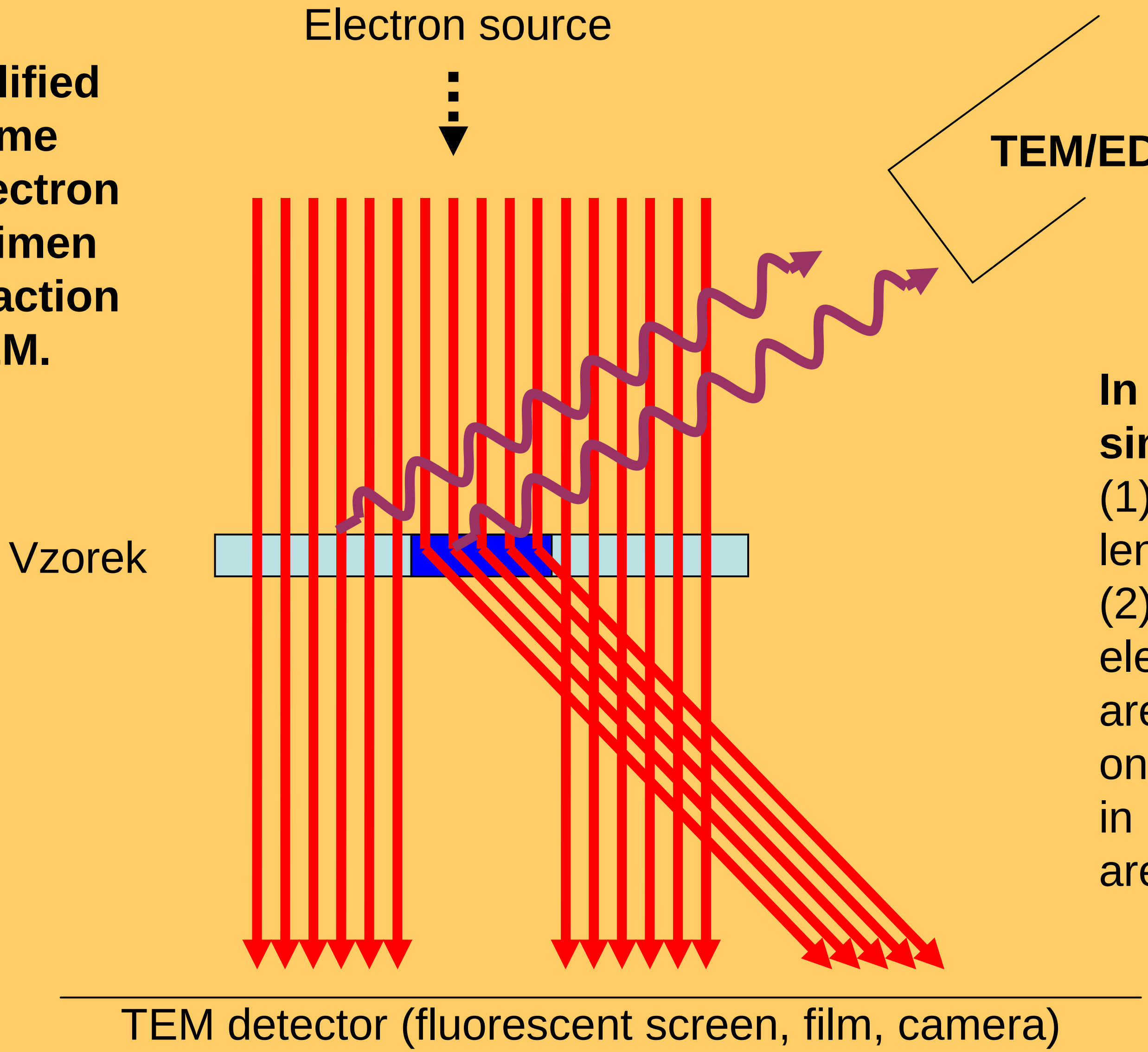
SEM: interaction of electrons and specimen at atomic level.



Methods of polymer morphology.

TEM: interaction of electrons and specimen.

Very simplified scheme of electron specimen interaction in TEM.



$\Rightarrow$ detector for **TEM/BF, TEM/DF, TEM/ED**

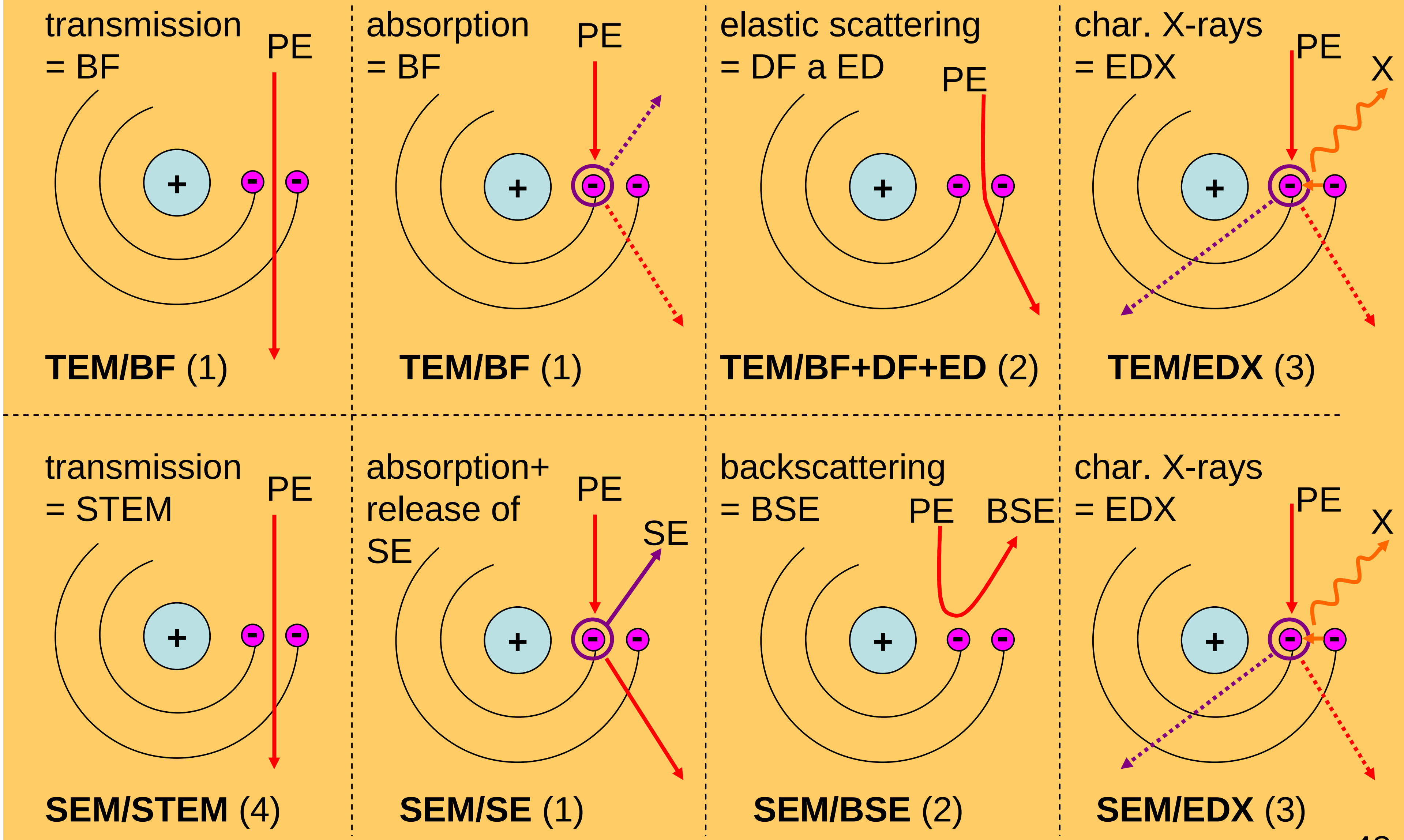
In which is the scheme simplified?

(1) Apertures and lenses are excluded.

(2) Path of diffracted electrons and X-rays are shown for just one direction; in reality, all directions are possible.

Methods of polymer morphology.

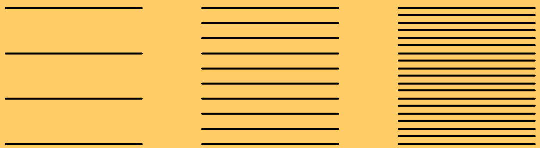
TEM: interaction of electrons and specimen at atomic level.



Methods of polymer morphology.

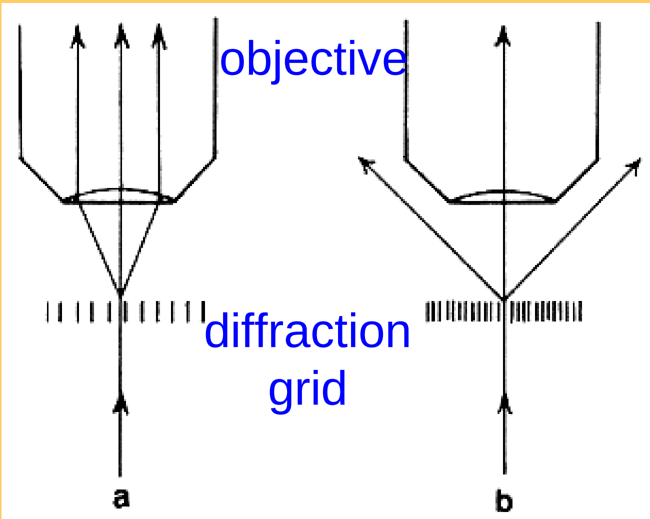
TEM: resolution in TEM (and LM).

What is resolution?

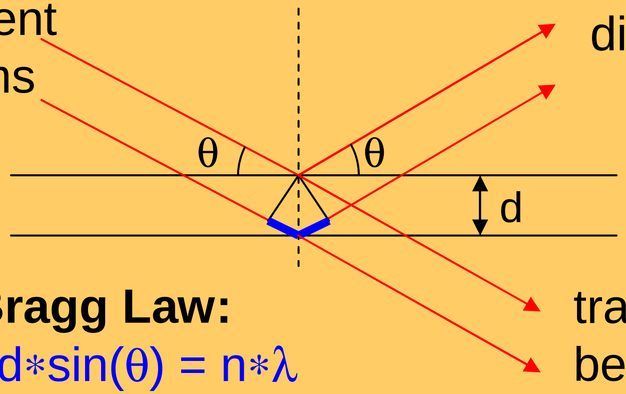


Resolution can be defined as an ability to differentiate neighboring lines in a diffraction grid.

How in a microscope?



Connection [resolution - diffraction]?



Bragg Law:

$2d*\sin(\theta) = n*\lambda$

Conclusion:

At low distances **d** big diffraction angles **θ**.

In a microscope:

[1] To distinguish lines at distance **d**, we have to catch diffracted beam ad angle **θ**.

[2] At very low **d** the beam goes out of objective, and so it cannot be detected.

[3] With an infinitely large objective we would catch at most beam at θ=90°: $2d*\sin(90^o) = 1*\lambda$

Max.resolution ≈ diffraction limit: d = λ/2

UNESCO/IUPAC Postgraduate Course in Polymer Science

Thank you for your attention.

- Institute of Macromolecular Chemistry ASCR, Heyrovsky sq. 2, Prague -162 06
- http://www.imc.cas.cz/unesco/index.html
- unesco.course@imc.cas.cz