

Vorlesung zum Haupt/Masterstudiengang Physik

Methoden Moderner Röntgenphysik II: Struktur und Dynamik Kondensierter Materie

Surfaces

(OHS)

Applications in Soft Matter

(MMAK / SVR)

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Applications in Soft Matter

- 20.04.2010 An Introduction to Polymer Physics
- 22.04.2010 **Small-Angle X-ray Scattering and its Applications**
- 27.04.2010 Polymer, Colloidal and Nanocomposite Surfaces I
- 29.04.2010 Polymer, Colloidal and Nanocomposite Surfaces II

Aim:

Overview over using X-ray scattering to understand soft matter

Why Polymers???



Automotive industry



Electronics



Soaps/detergent



Medicine



Packaging industry



1. **Commodity polymers:** plastic shapes, packaging, bottles for beverages...

PMMA, PS, PE, PP, PET,...

2. **High-performance polymers:** outstanding chemical resistance and/or mechanical properties, heat resistance

PTFE, PVDF, PEEK, polyimides,...

3. **Functional polymers:** tailor-made molecular architecture results in specific optoelectronic properties and “smart” behavior

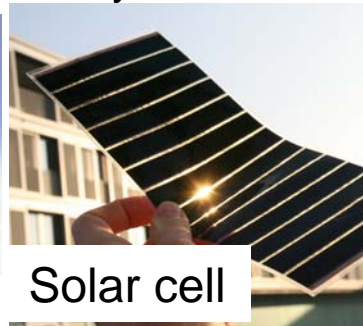
Materials for nanotechnology

4. **Biopolymer:** found in nature, replacing the commodity and functional polymers

starch, protein, DNA, RNA



Textile industry

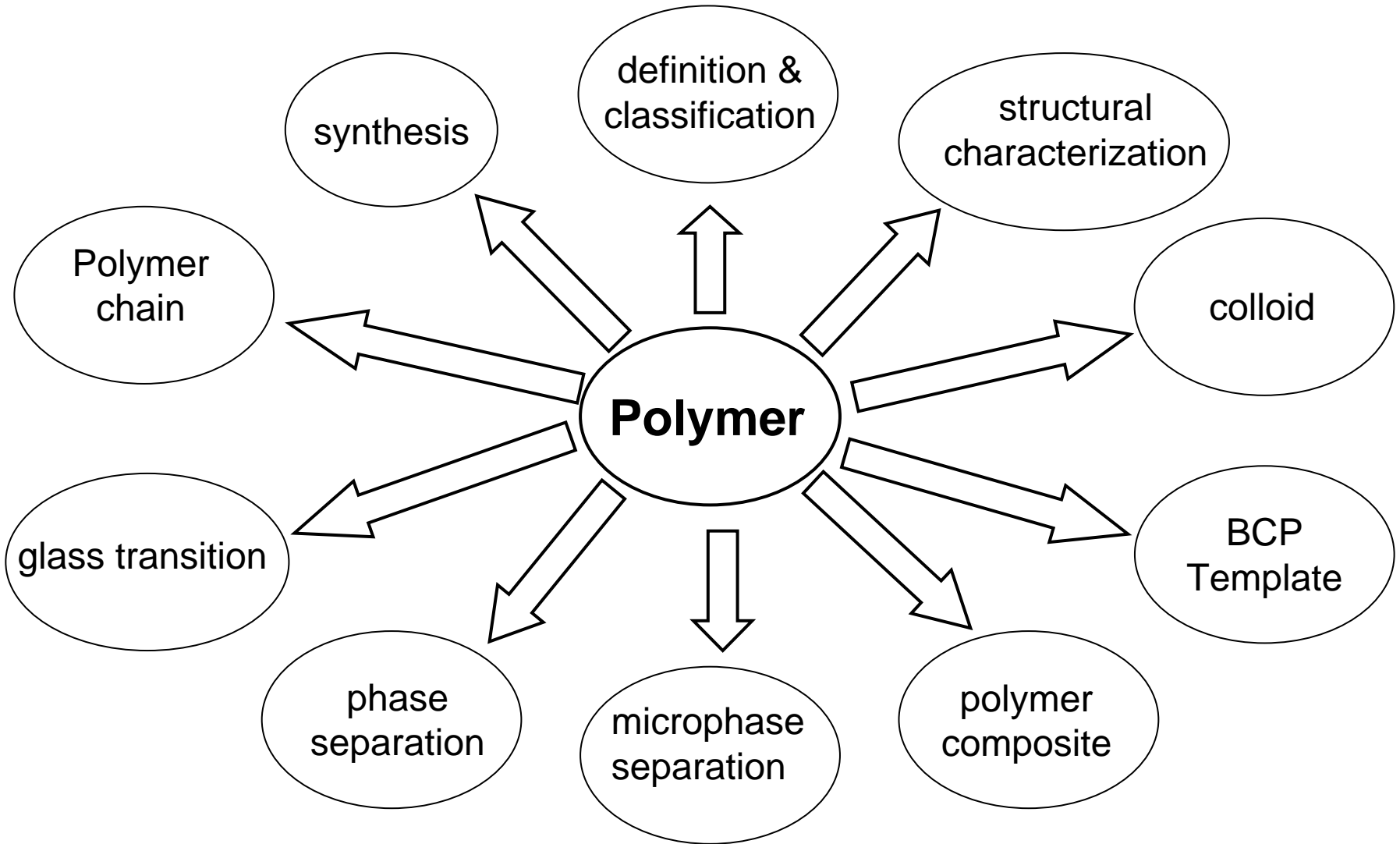


Solar cell

Flexible properties and diverse application!!!

Why?

An Introduction to Polymer Physics



Literature

Physics

U. W. Gedde: *Polymer Physics*; Chapman&Hall, London (1995), ISBN 0-412-59020-4

G. Strobl: *The Physics of Polymers*; Springer Verlag, Berlin (1997), ISBN 3-540-60768-4

22. IFF-Ferienkurs: *Physik der Polymere*; Forschungszentrum Jülich (1991), ISBN 3-89336-055-7

D. I. Bower: *An Introduction to Polymer Physics*; Cambridge University Press (2002), ISBN 0-521-63721-X (Paperback)

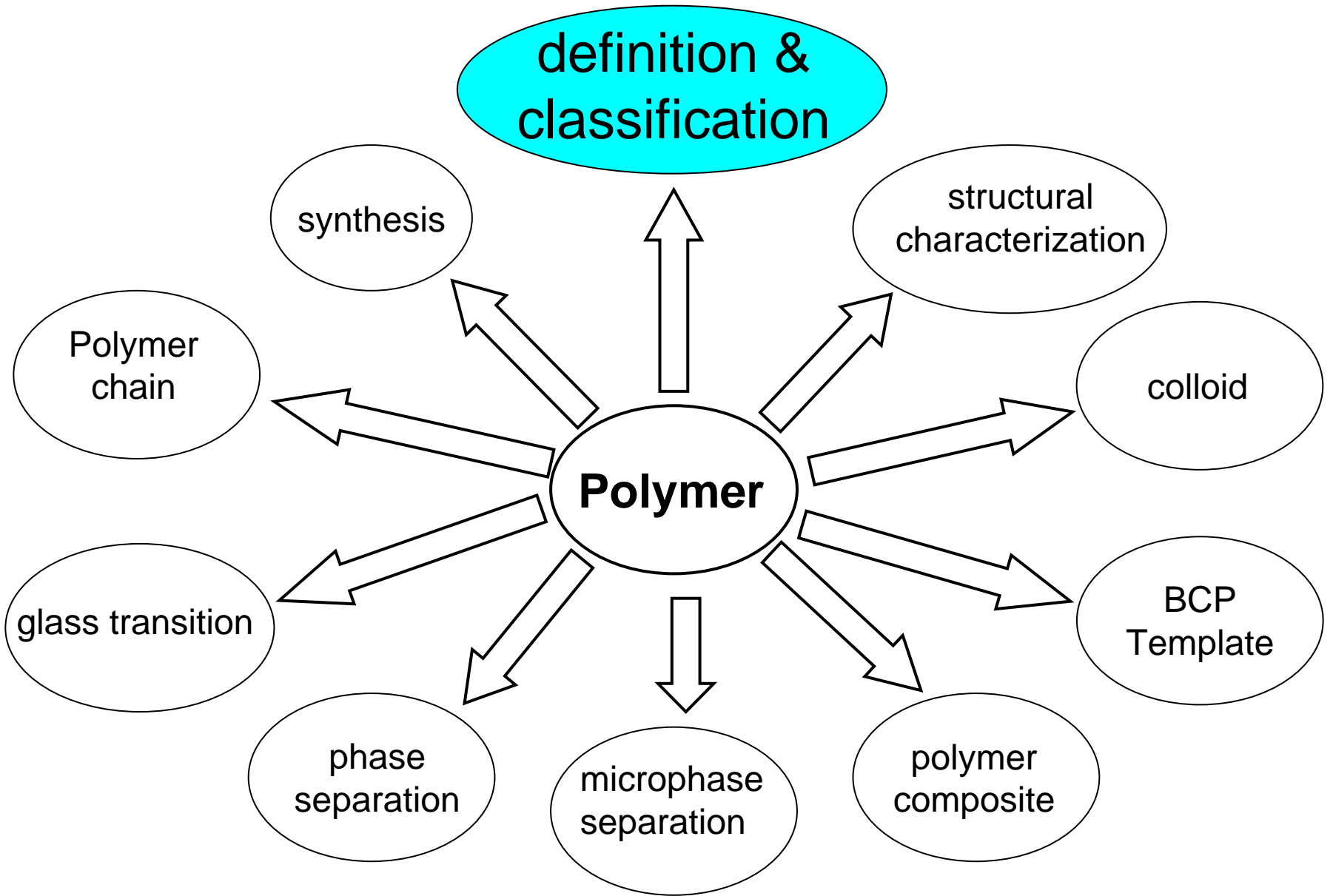
Chemistry

C. E. Carraher: *Seymour/Carraher's Polymer Chemistry*; Marcel Dekker, New York (2000), ISBN 0-8247-0362-6

Material Sciences

H.-G. Elias: *An introduction to polymer science*; VCH, New York (1997), ISBN 3-527-28790-6

G. H. Michler: *Kunststoffmikromechanik*; Hanser, München (1992), ISBN 3-446-17068-5



basic definitions

Polymer: *polys* --- many, *meros*---parts : Macromolecules built up of a large number of molecular units that are linked together by covalent bonds. Usually they represent organic compounds, containing carbon atoms together with hydrogen, nitrogen, and halogens, etc.

According to the IUPAC (*International Union of Pure and Applied Chemistry*) *Polymer is a substance composed of macromolecules. A macromolecule is a molecule having high relative molar mass, the structure of which essentially comprises the multiple repetitions of units derived, actually or conceptually, from molecules of low relative molecular mass.*

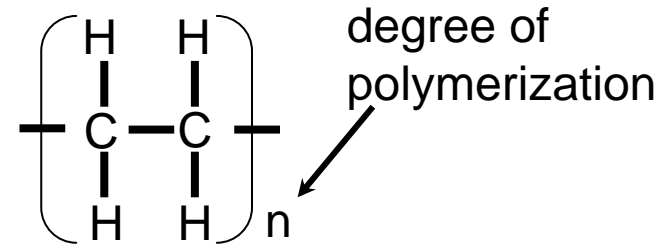
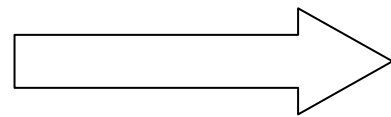
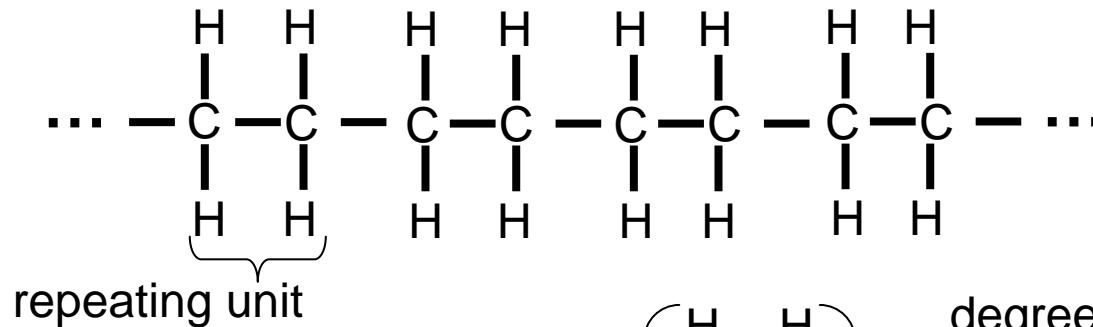
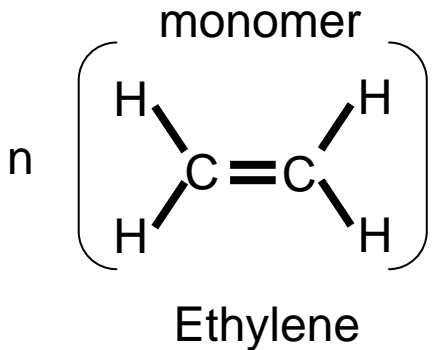
To distinguish polymers from other chain molecules scientists use quite often one general classification of molecules based on their molecular weight, M_W . This classification is following:

- Micromolecule with $M_W < 1,000$ g/mol
- Oligomer with $M_W \approx 1,000 - 10,000$ g/mol
- Polymer with $M_W > 10,000$ g/mol

basic definitions

Monomer: Chemically identical small molecules having the potential of chemically binding to other monomers of the same species to form a Polymer.

Standard example: Polyethylene (PE)



Polyethylene (PE)

Polymerization: polymerization is a process of reacting monomers together to form a higher molar mass polymer chains.

Degree of polymerization: The number of monomer units present in one single polymer chain is called degree of polymerization and denoted often as N.

basic definitions

Molecular weight

- Polymerization reaction yields macromolecules of different chain length!!!
- The molar mass of polymer is characterized by the molar mass distribution function.

M -----Molar mass

$\rho(M)$ -----Number density distribution function

Normalizing $\int_0^{\infty} \rho(M) dM = 1$

- Number average molecular weight:

$$\overline{M}_N = \int_0^{\infty} \rho(M) M dM$$

- Weight average molecular weight:

$$\overline{M}_W = \frac{\int_0^{\infty} \rho(M) M \cdot M dM}{\int_0^{\infty} \rho(M) M dM}$$

- Weight fraction $\rho' = \frac{\int_0^{\infty} \rho M}{\int_0^{\infty} \rho(M) M dM}$

basic definitions

Note: $\overline{M}_w > \overline{M}_n$

- Polydispersity:
$$P = \frac{\overline{M}_w}{\overline{M}_n}$$

- Polydispersity coefficient /index

$$U = \frac{\overline{M}_w}{\overline{M}_n} - 1$$

- Centrifugal average or Z-average \overline{M}_z
- Viscosity average \overline{M}_η

Molar mass distribution function

- **Schulz-Zimm** \Rightarrow step polymerisation (polycondensation)

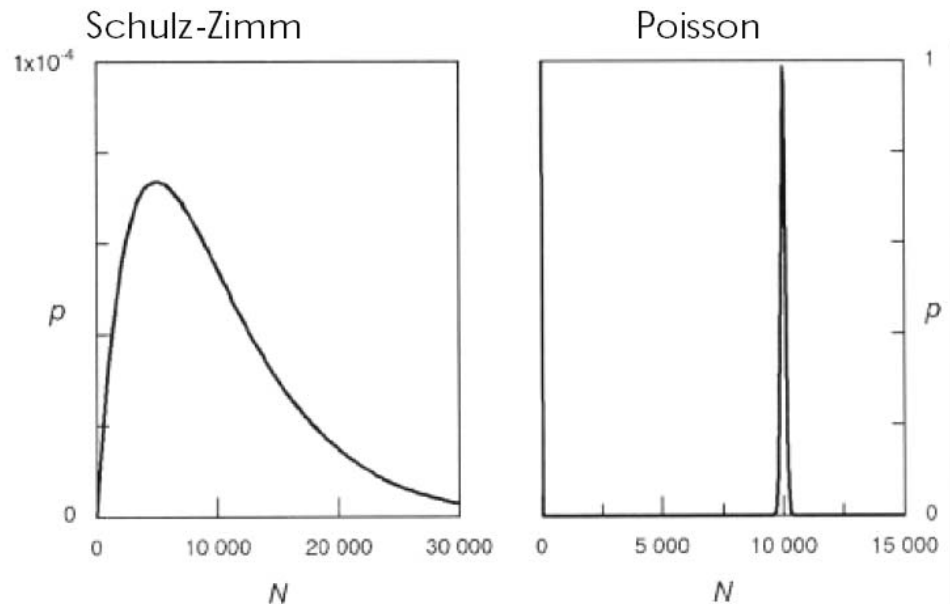
$$p(N) = \frac{1}{\Gamma(\beta)} \left(\frac{\beta}{\overline{N}_n} \right)^\beta \cdot N^{\beta-1} \exp - \frac{\beta N}{\overline{N}_n} \quad \Rightarrow \quad U = \frac{1}{\beta}$$

- **Poisson** \Rightarrow chain polymerisation (anion)

$$p(N) = \exp - \frac{N}{\overline{N}_n} \cdot \frac{(\overline{N}_n)^N}{\Gamma(N+1)} \approx \exp - \frac{N}{\overline{N}_n} \left(\frac{\overline{N}_n e}{N} \right)^N \quad \Rightarrow \quad U = \frac{1}{\overline{N}_n}$$

β determines the shape

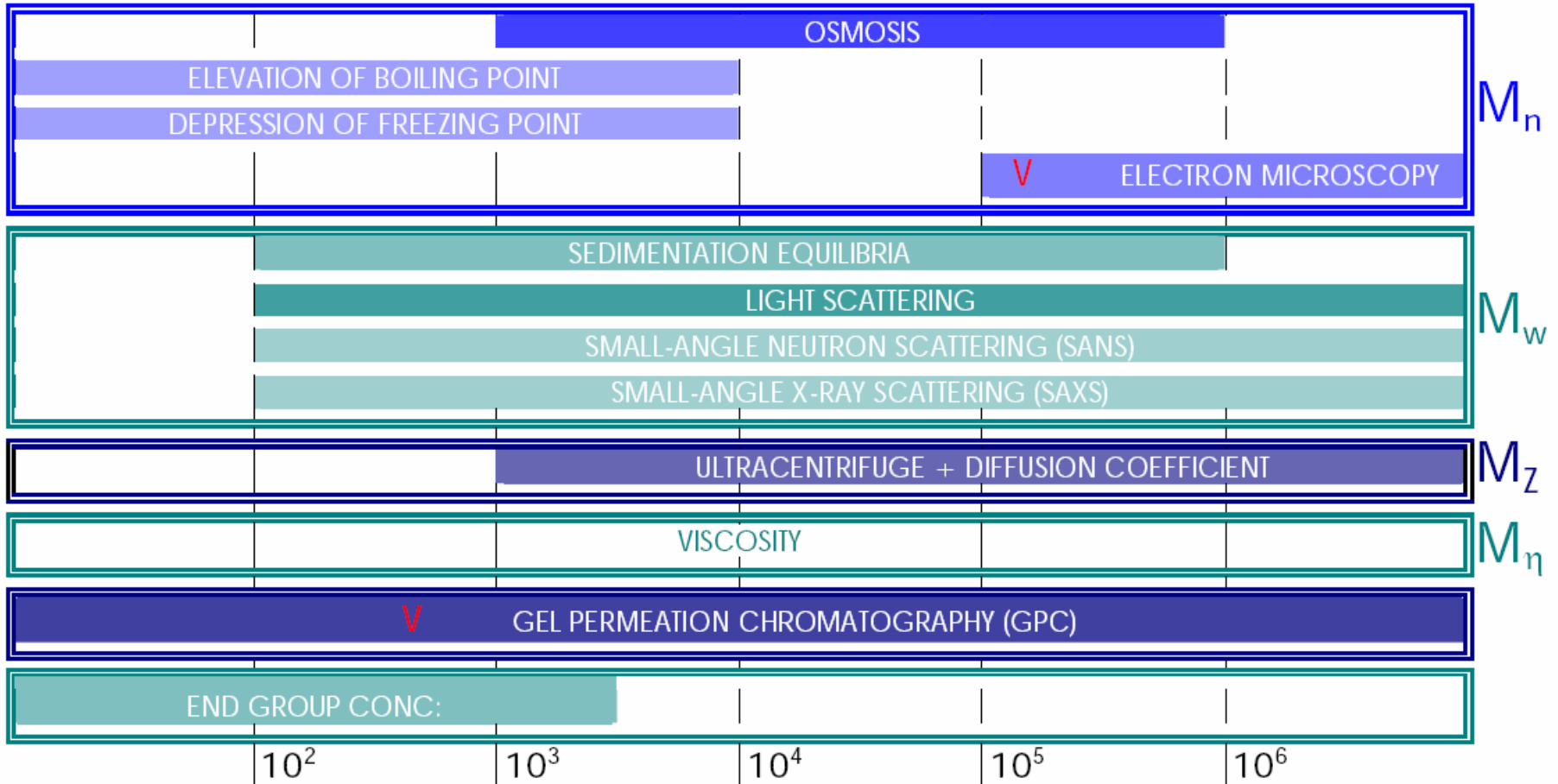
\overline{N}_n Number average degree of polymerization



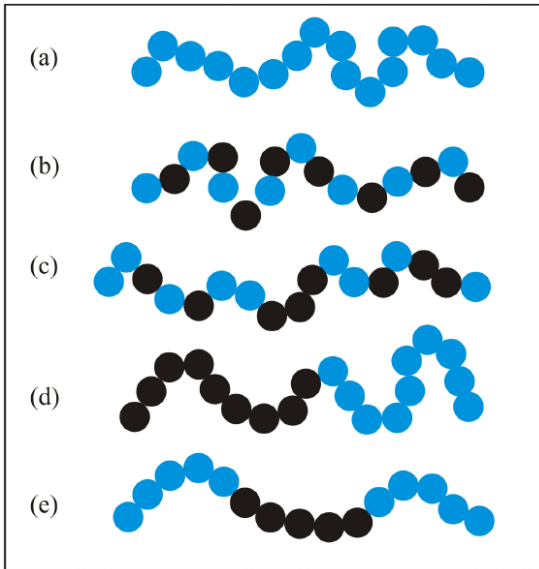
$$\beta = 2$$

$$\overline{N}_n = 10,000$$

Molecular weight determination



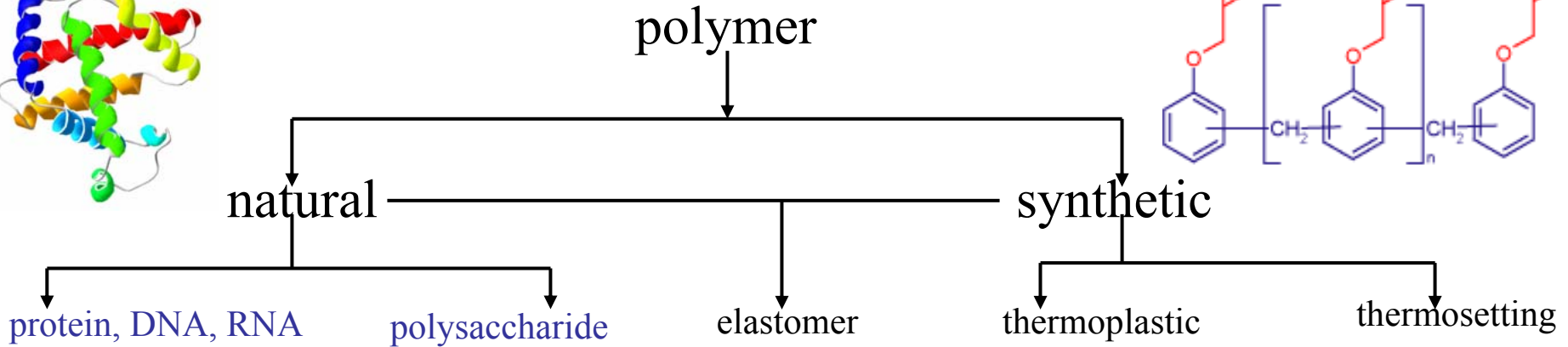
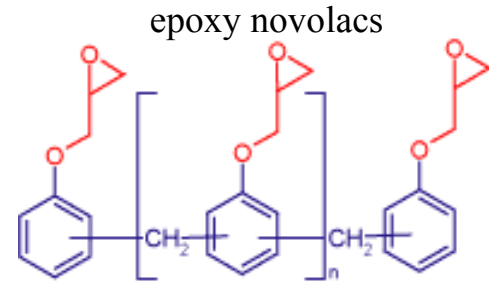
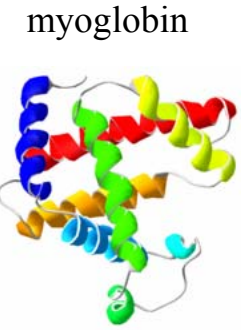
Nomenclature



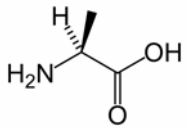
- According to the basic repeating unit, e.g.
 Polypropylene - **PP**, Poly(methylmethacrylate) – **PMMA**,
 Polystyrene - **PS**, Poly(ethylene terephthalate) – **PET**,
 Poly(p-phenyleneterephthalamide) – **PPTA**
- trade names: **Kevlar**, **Nylon**, **Aramid**, **Plexiglas** etc.
- IUPAC: Poly (1-phenyl ethylene) -- **PS**

Type		Example
Homopolymer (a)		PolyA
Not specific	-co-	Poly(A-co-B)
Statistical	-stat-	Poly(A-stat-B)
Random (c)	-ran-	Poly(A-ran-B)
Periodic	-per-	Poly(A-per-B)
Alternating (b)	-alt-	Poly(A-alt-B)
Network	net-	Net-Poly A
Diblock (d)	-b-	Poly (A-b-B)
Triblock (e)	-b-	Poly (A-b-B-b-A)

Classification

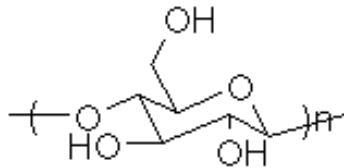


(amino acid sequence)



L-alanine

(sugar unit)



cellulose

starch, glycogen,
chitin, gums, resin

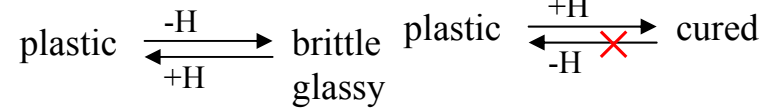
natural rubber,
butyl rubber,
nitrile rubber,
SBR, Silicone,
EPM, resilin



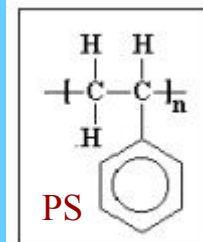
no cross-links



Elastomer
cross-linked

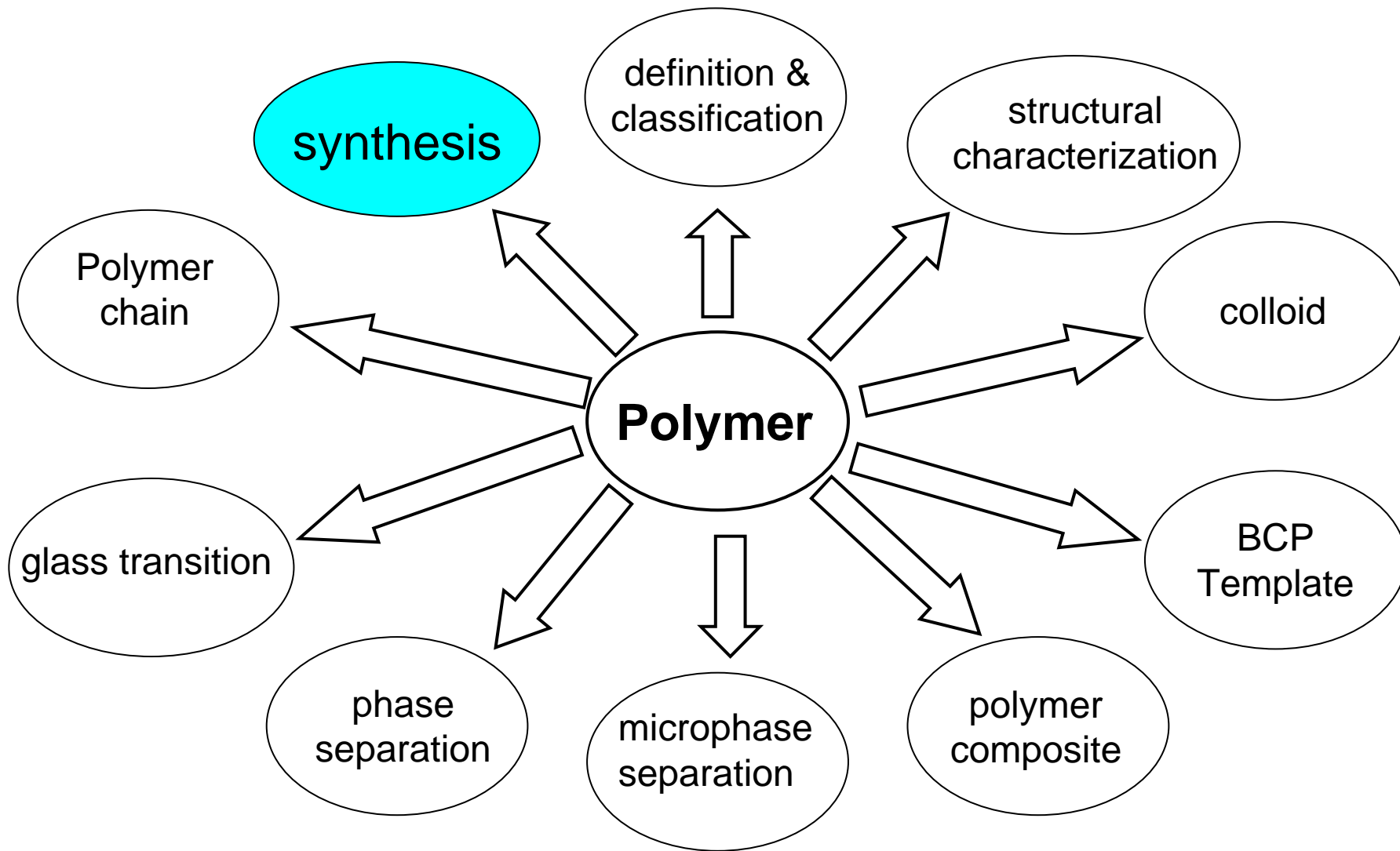


PE, PP, PC, PB,
polyester, PS,
PVC, PTFE,
celluloid,
cellulose acetate



PS

vulcanized rubber
duroplast, bakelite,
melamine, epoxy
resin, urea-
formaldehyde



Polymer synthesis

Chain-growth Polymerization:

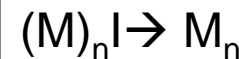
1. **Initiation**: Initiator initiates the chemical reaction by breaking the unsaturated bonds. Peroxides (-O-O-), disulfides (-S-S-) and Azo (-N=N-) compounds are typical initiators



2. **Propagation**: increase of chain length

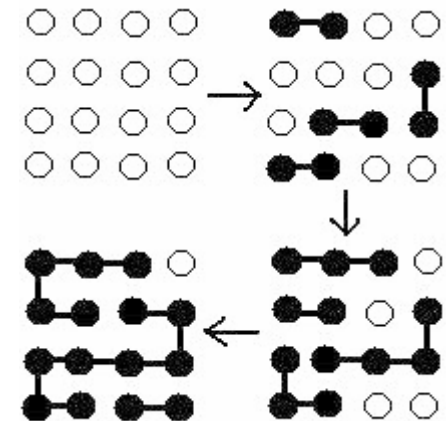


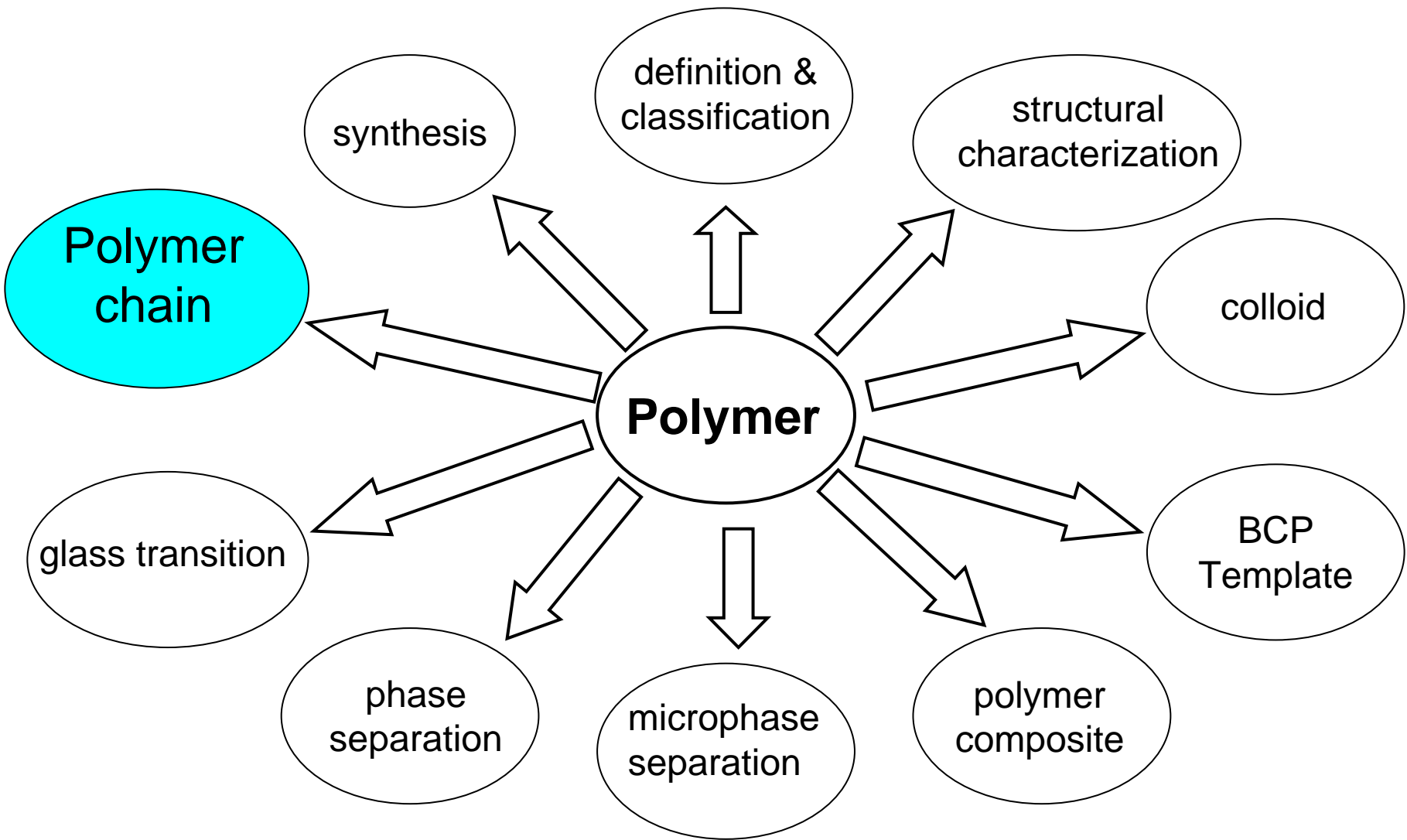
3. **Termination**: combination or disproportionation of free radicals



Step-growth Polymerization:

- bifunctional or multifunctional monomers react to form dimers, trimers, longer oligomers and long chain polymers, e.g; esters (Polyesters), amines & esters (Polyamide).

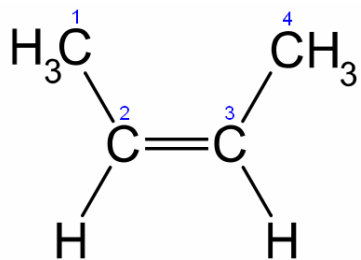




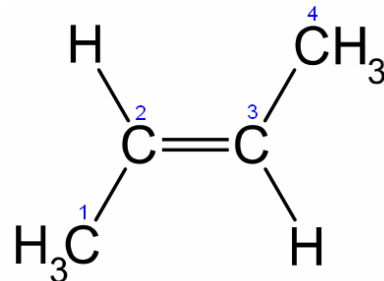
The polymer chain

Configuration and conformation

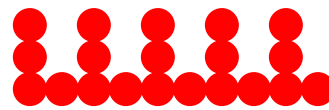
Configuration refers to the order that is determined by chemical bonds. The configuration of a polymer cannot be altered unless chemical bonds are broken and reformed. The two types of polymer configurations are *cis* and *trans*. The *cis* configuration arises when substituent groups are on the same side of a carbon-carbon double bond. *Trans* refers to the substituents on opposite sides of the double bond. Arrangement of the side chains (steric order) present in the main chain of a polymer is called **tacticity**. Polymers with a unique way of coupling of the monomeric units are called **isotactic** and with an irregular steric structure, called as **atactic**. If the coupling varies, in a regular way, polymer chains are called **syndiotactic**. Tacticity is very important in polymer thermodynamics.



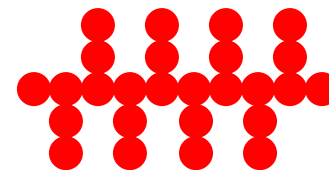
cis-2 butene



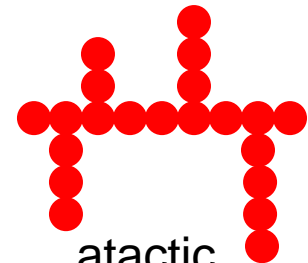
trans-2 butene



isotactic



syndiotactic



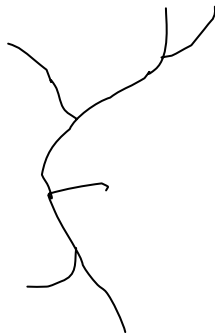
atactic

The polymer chain

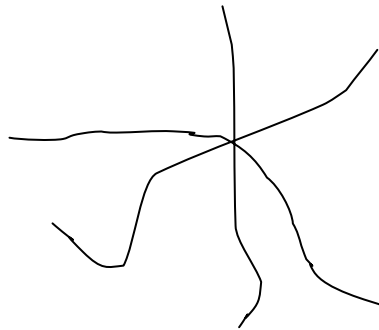
Configuration and conformation

Configurations that arise due to the rotation of two atoms, bonded by a single bond, relative to each other are called **conformations**. Three generalized types of conformations based on the potential energy as a function of torsional angle are **anti** (trans), **eclipsed** (cis) and **gauche** (+ or -).

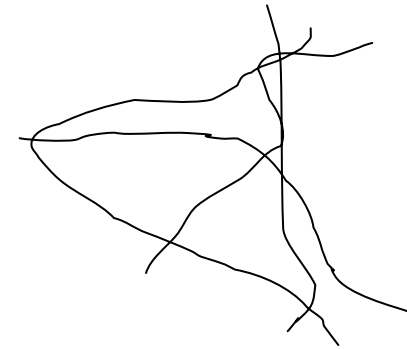
Chain architecture



Short chain and
Long chain branches

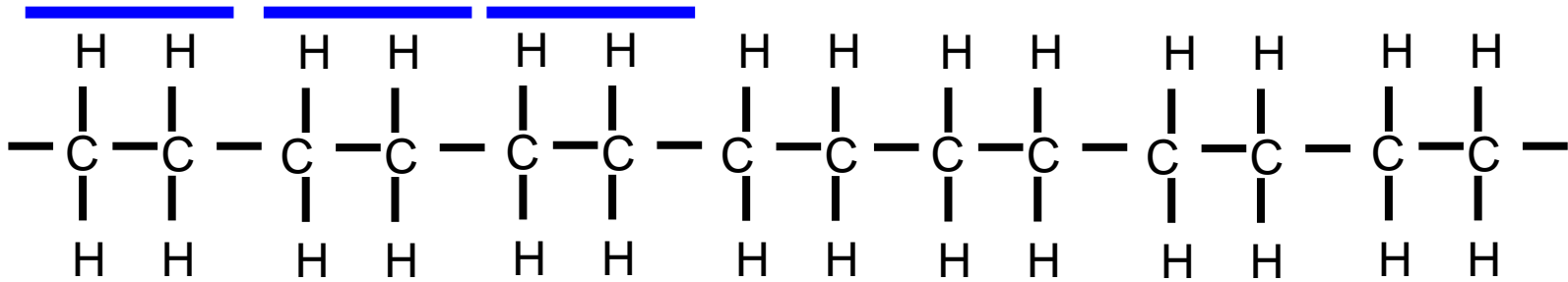


Star polymers

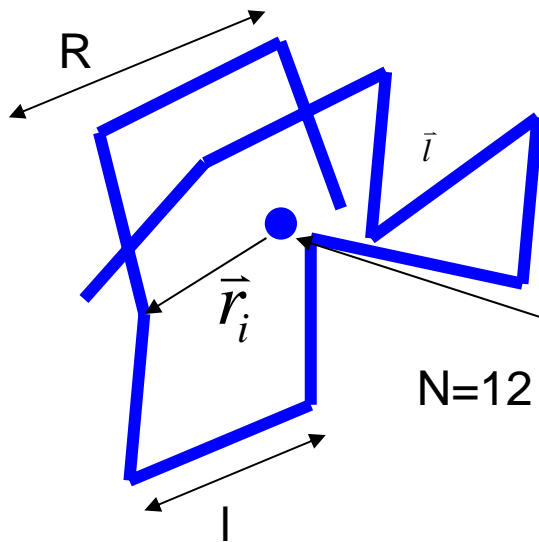


Network of cross-
linked chains

The polymer chain



Linear chains exist, but more realistically:
Rotational degree of freedom



Mean segment length $\bar{l} =$

Contour length path length $L = 12 \cdot |\bar{l}|$

End-to-end distance R

Center of gravity



The polymer chain

End-to-end distance: $R = \sqrt{N} \cdot \sqrt{\langle |\vec{l}|^2 \rangle} = \sqrt{N} \cdot l$

$$R_G = \sqrt{\frac{1}{M} \sum_1^N \langle m_i \vec{r}_i^2 \rangle}$$

M mass of macromolecule
 m_i mass of segment

Mean over all configurations

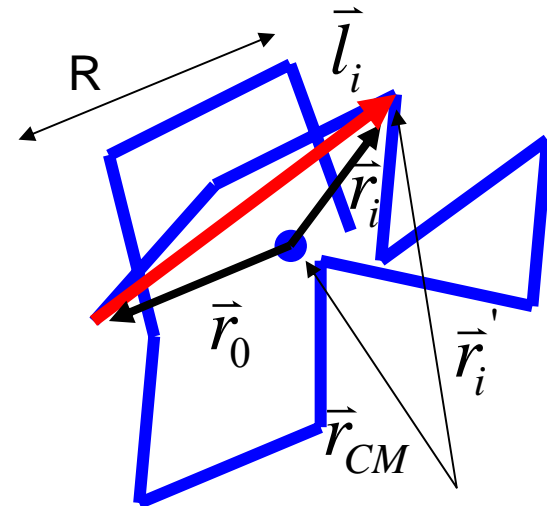
Radius of gyration (for a gaussian, uncorrelated chain)



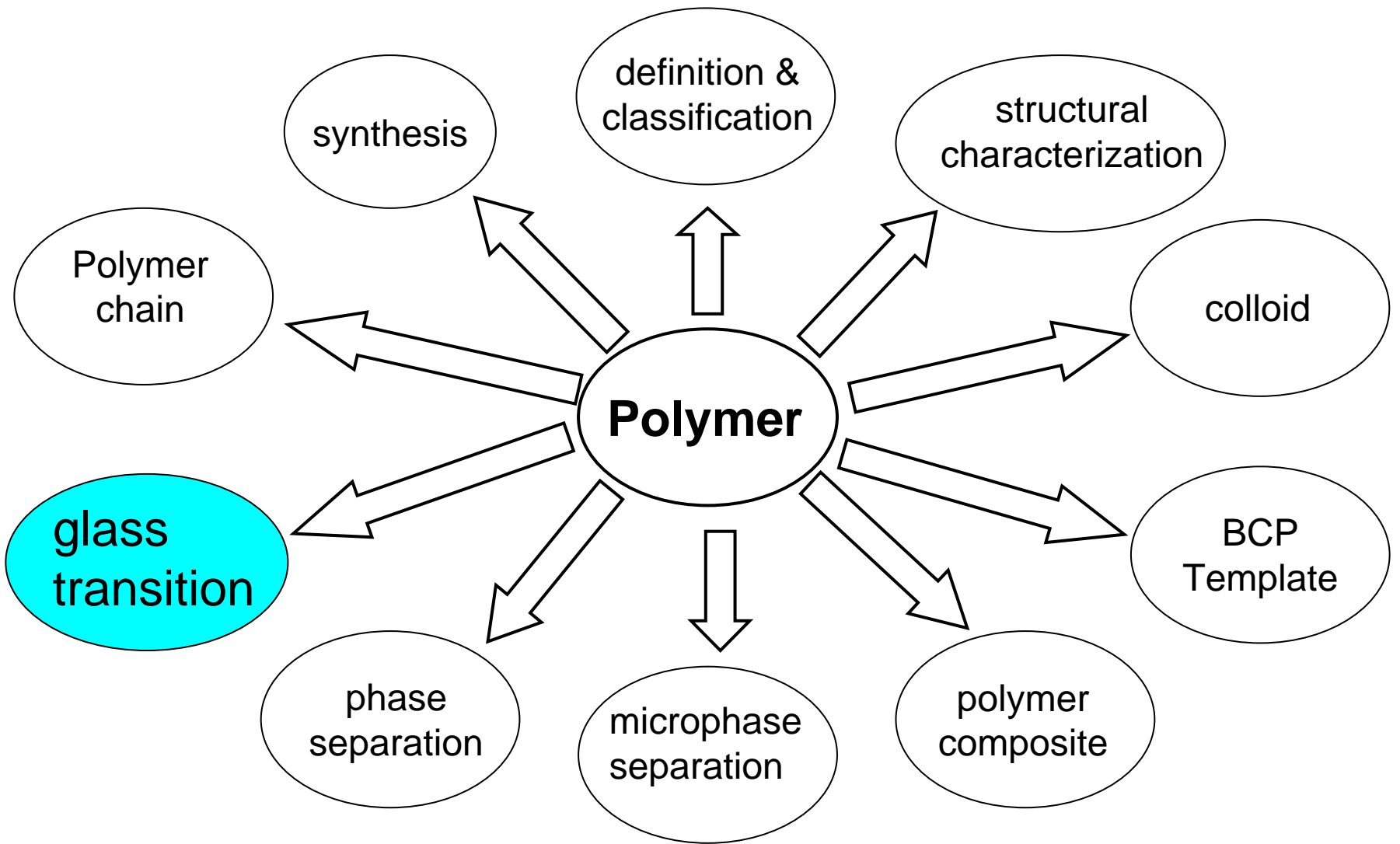
Measure for extension of macromolecule

Relation between R_G and R $R_G^2 = R^2 / 6$

Using $\vec{r}_i = \vec{r}_0 + \vec{l}_i = \vec{r}_i' - \vec{r}_{CM}$



We will need this for small angle x-ray scattering!



Glass transition

... more during part II, summer semester lectures (Hermann Franz)

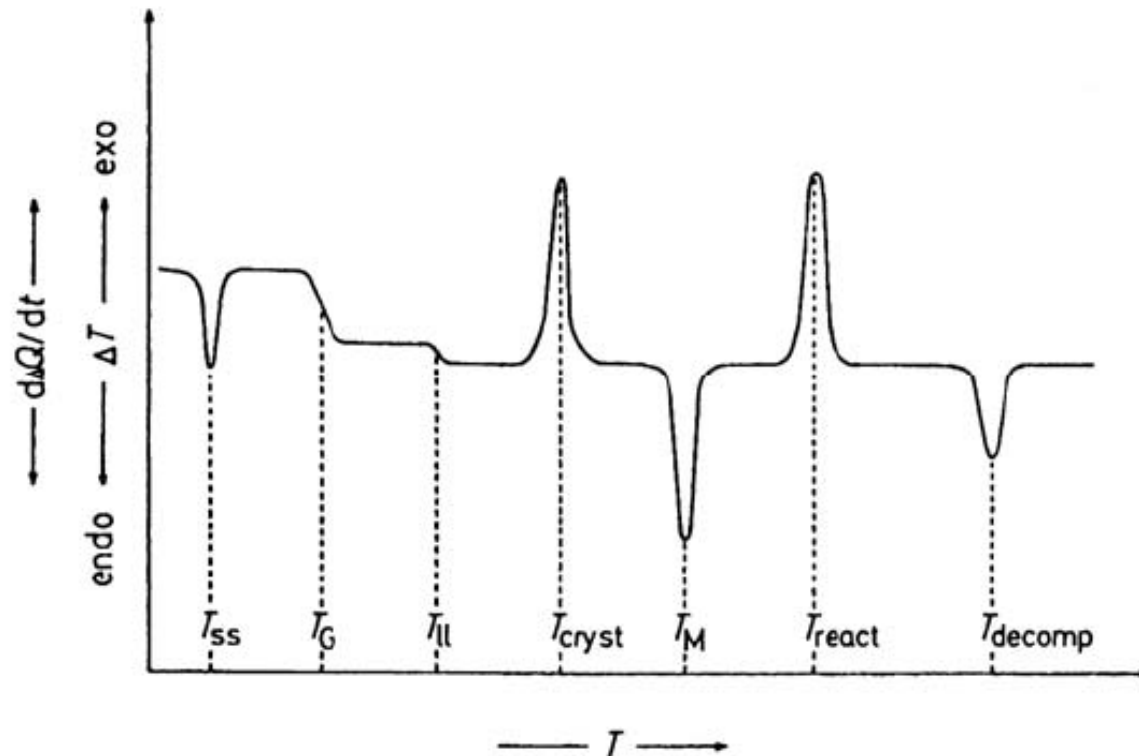
Brief introduction – important to understand structure of thin films!

The **glass transition** is a very important physical property of amorphous polymers. It is characterized by the **temperature** above which the polymer starts **flowing** like rubber and below this temperature the polymer behaves like a **supercooled liquid** (for example **glass**). Since it is the **transition of polymer between rubbery state and glassy state**, it is called the glass transition temperature. It is denoted by **T_g**. This temperature is determined usually by differential scanning calorimetry (DSC).

- **the molecular theory** : The polymer chains have a great deal of freedom of mobility to take all possible conformation allowed by the rotation around the single bonds at temperature well above T_g. At temperature well below T_g all these conformations are frozen out and the polymer acts like a glassy solid.
- **the free-volume theory**: If the conformational changes of the backbone are to take place, there must be available free space for the molecular segments to move into. As the temperature is lowered from a temperature well above T_g, the molecules are able to rearrange locally to reduce the free volume. When the temperature approaches T_g the molecular motion becomes so slow that the molecules can not rearrange within the time-scale of the experiment and the volume of the material then contracts like that of a solid.

Tg determination

Differential scanning calorimetry (DSC): heat capacity as a function of temperature



Thermogravimetry (TGA)

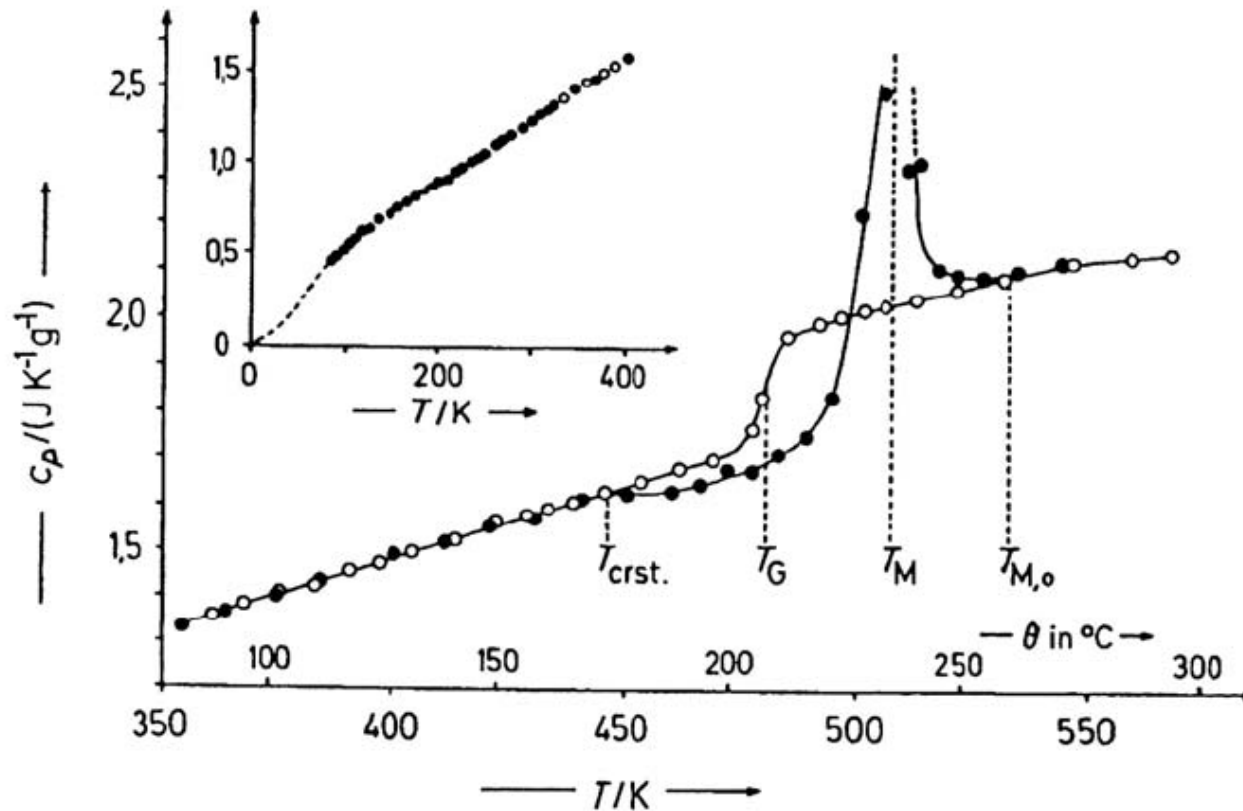
Differential thermal analysis (DTA)

Thermomechanical analysis (TMA)

Heating and cooling rate $\sim 10^\circ\text{C}/\text{min}$

Tg determination

Typical DSC data for semicrystalline (filled circle) and amorphous polymer

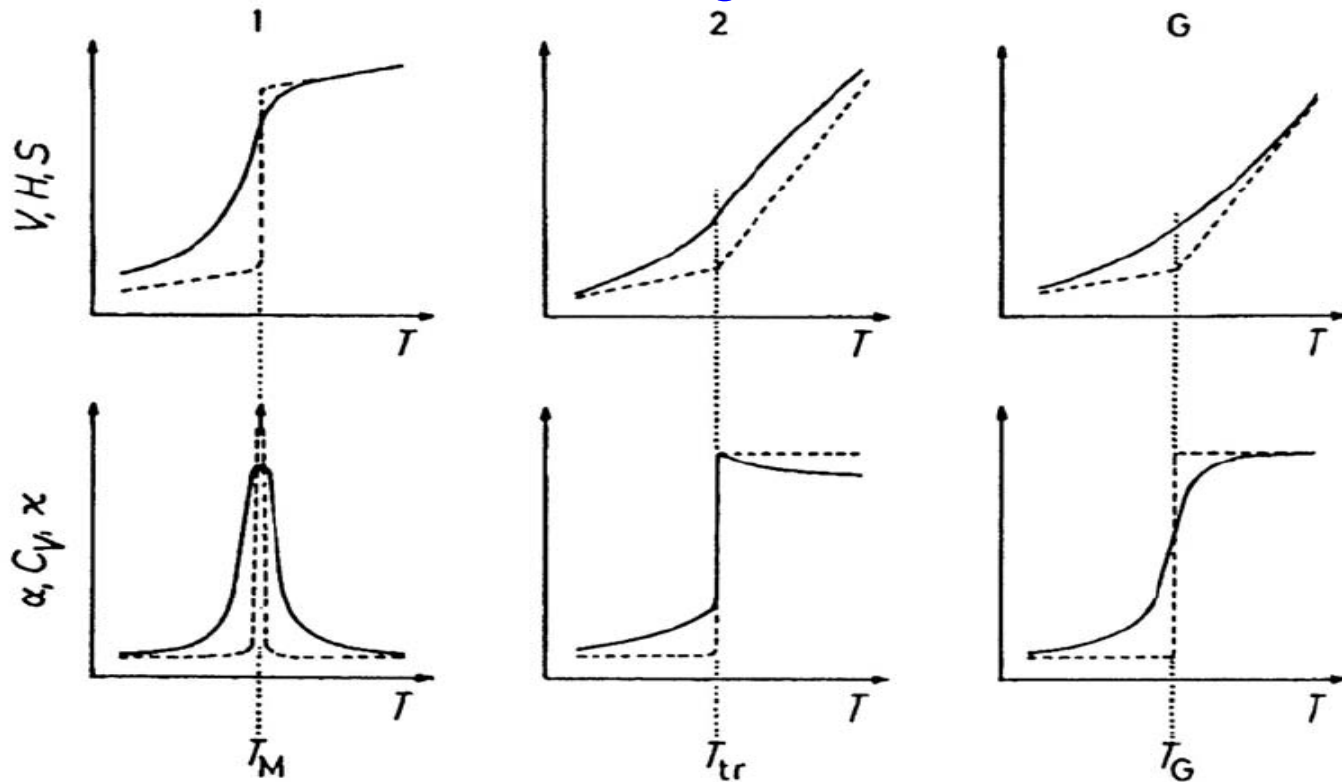


PS : 104 $^\circ\text{C}$

PB : -109 $^\circ\text{C}$

PBMA : 35 $^\circ\text{C}$

Phase transition vs. glass transition

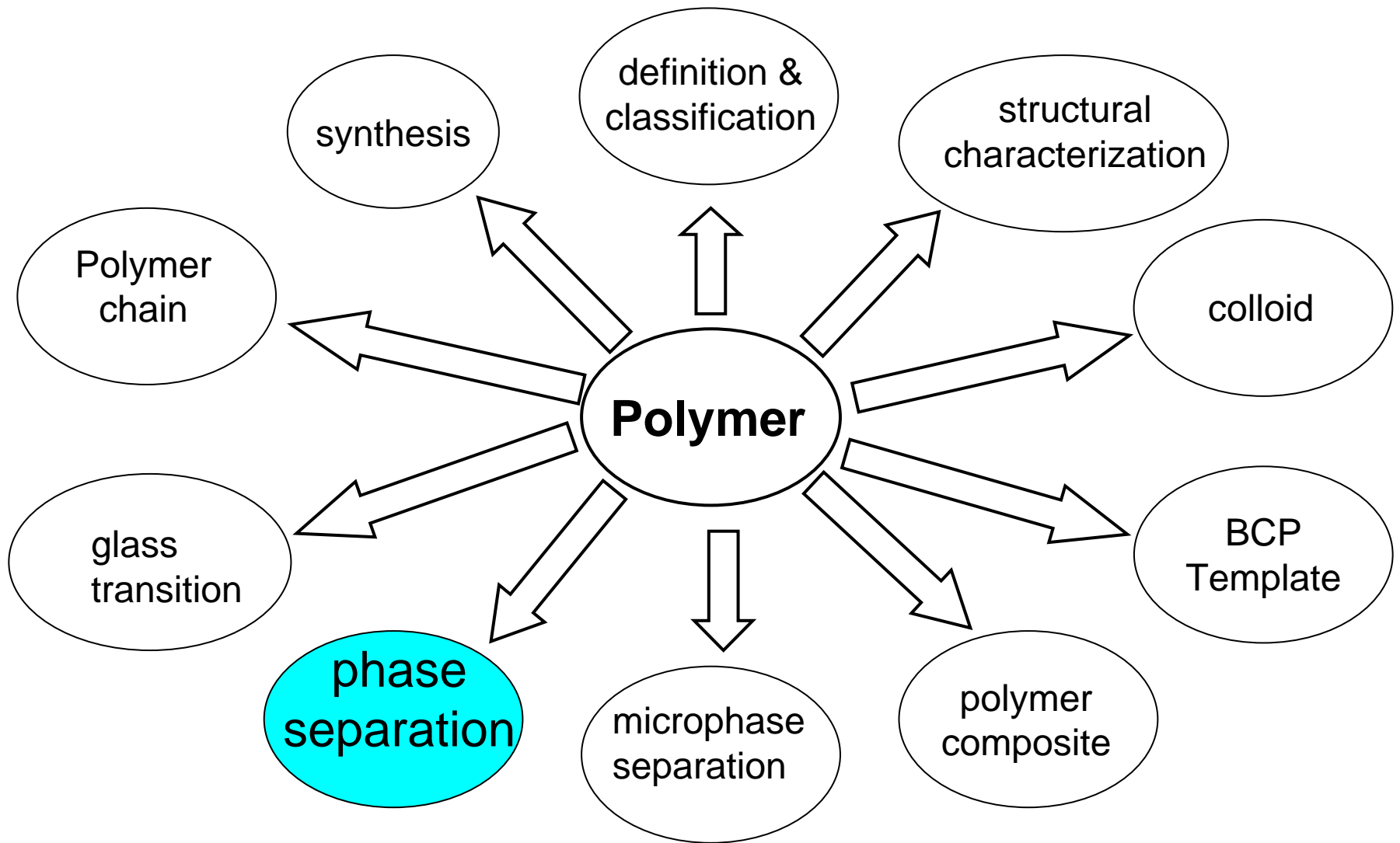


1st order phase transition:
Melt of Crystal with or
without defect

2nd order phase transition:
intermolecular cooperative
effect

glass transition: infinite
process. Normal
experiment. Endless slow.

Glass transition is not a thermodynamic equilibrium state!!!



Phase separation

Polymer blends → mixing of two more homopolymers
→ a route to combine different materials properties

High fracture resistance and stiff

Problem: increase in elastic moduli → brittle

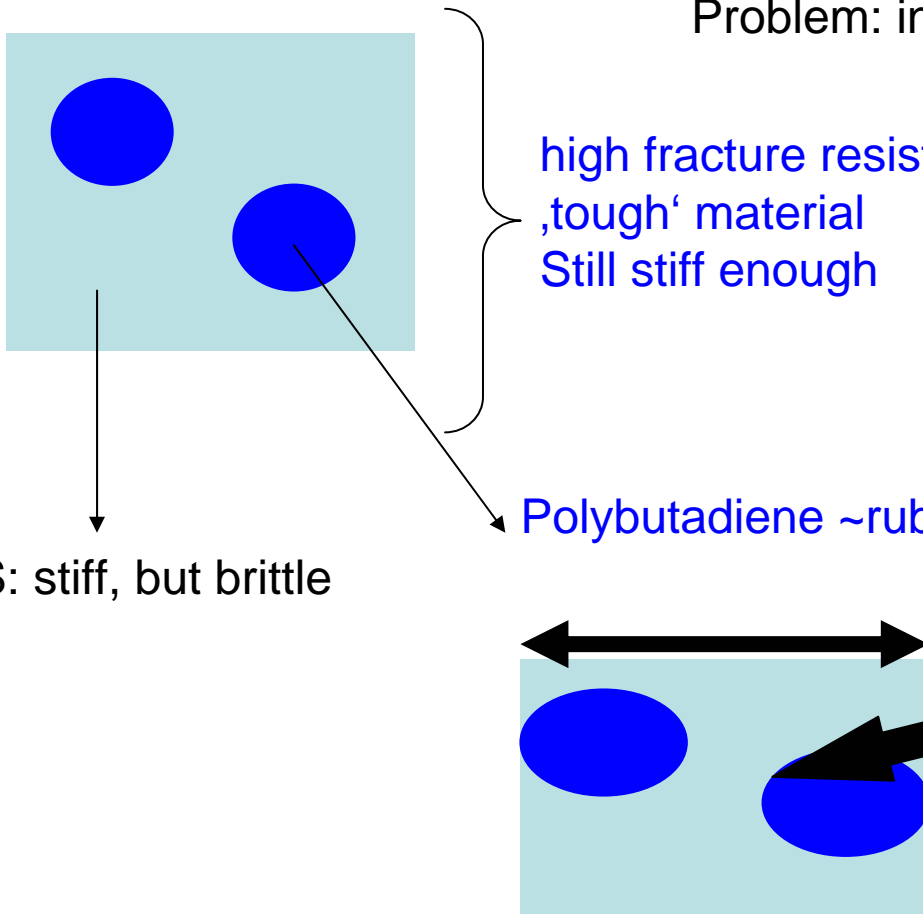
high fracture resistance
,tough' material
Still stiff enough

Polybutadiene ~rubber

PS: stiff, but brittle

Fracture starts here and is initially localized here!

We can investigate deformation and crack propagation with X-ray scattering!



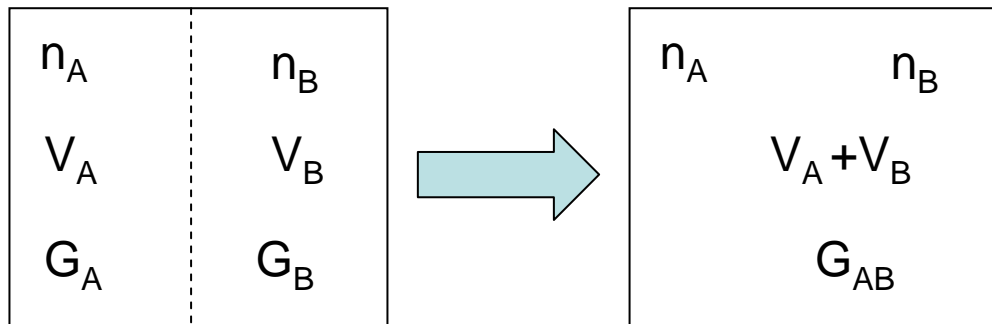
Phase separation

Flory-Huggins-Theory

Q: when do we obtain a homogenous or heterogenous morphology during blending?

A: Flory-Huggins theory – phase diagrams as function of T and M:

When can we expect single, binary... phases



Reminder:
$$dG = -SdT + Vdp + \underbrace{\mu dN} + \gamma dA$$

S... entropy

μ ... chemical potential (keyword: diffusion), change in phase: equilibrium $\mu_1 = \mu_2$

γ ... surface tension (2D)

For mixing:
$$\Delta G_{mix} = G_{AB} - (G_A + G_B)$$

Phase separation

Flory-Huggins-Theory

It states:

$$\Delta G_{mix} = -T\Delta S_t + \Delta G_{loc}$$

Change in entropy:
Mixing → increase

Associated with motions of
center of mass of all polymer
molecules

+ : favours mixing

Change of local interactions and motion of
monomers

General rule: Van-der-Waals interactions
→ attractive energies between equal
monomers are stronger than between
different ones

- : unfavorable for mixing

Change in V: Shrinking, expansion

Formulas?

Flory-Huggins-Theory

$$\Delta G_{mix} = -T\Delta S_t + \Delta G_{loc}$$

$$1) \quad \Delta S_t = Rn_A \ln \frac{V}{V_A} + Rn_B \ln \frac{V}{V_B} \quad \phi_{A,B} = \frac{V_{A,B}}{V}$$

$$\Delta S_t = -Rn_A \ln \phi_A - Rn_B \ln \phi_B$$

Assumption: Polymer chains ~ ideal gas

$$2) \quad \Delta G_{loc} = RT \frac{V}{v_C} \chi \phi_A \phi_B$$

v_C Molar volume of a reference unit common to A and B

„The higher the concentration, the more likely the interaction“

Empirical parameter χ Flory-Huggins-Parameter
Nearest neighbour interactions
„contact energies“

This makes sense:

$$\Delta G_{loc} \rightarrow 0$$
$$\phi_A, \phi_B \rightarrow 0$$

Flory-Huggins-Theory

$$\Delta G_{mix} = RTV \left(\frac{\phi_A}{v_A} \ln \phi_A + \frac{\phi_B}{v_B} \ln \phi_B + \frac{\chi}{v_C} \phi_A \phi_B \right) \quad v \quad \text{Molar volume}$$

Low molar mass \rightarrow entropy leads to mixing

Polymers: large molecular weights $v_{A,B} \rightarrow \infty$ $\Delta S_t \rightarrow 0$

Mixing takes place, when $\Delta G_{mix} < 0$

$\chi < 0$ Mixing! $\chi > 0$ incompatibility

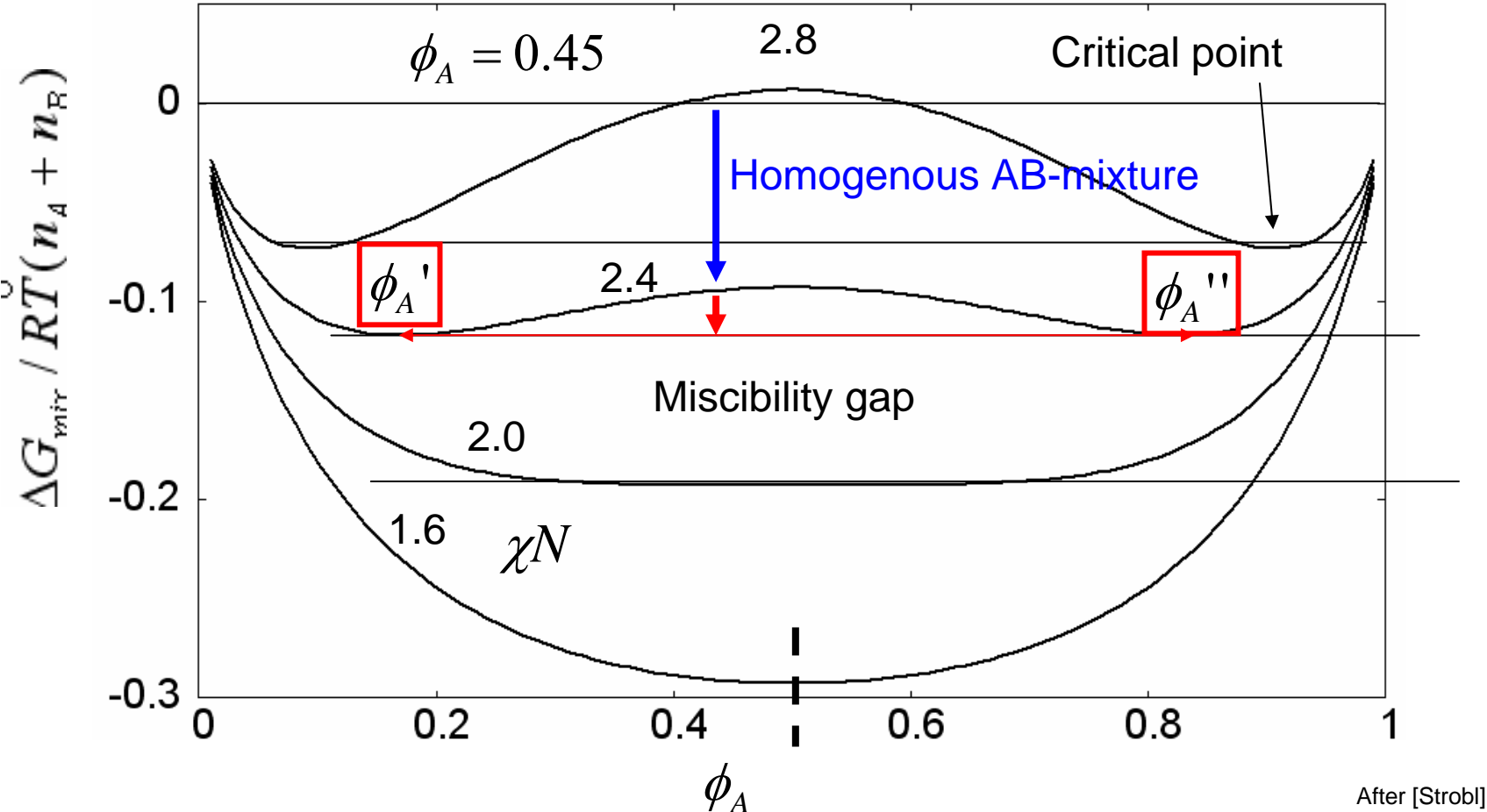
Symmetric mixture: Equal degree of polymerization

$$N_{A,B} = \frac{v_{A,B}}{v_C} \quad N_A = N_B = N \quad \phi_A + \phi_B = 1$$

$$\Delta G_{mix} = RT(n_A + n_B)(\phi_A \ln \phi_A + \phi_B \ln \phi_B + \chi N \phi_A \phi_B)$$

Phase separation

Symmetric binary polymer mixture



After [Strobl]

$\phi_A' < \phi_A < \phi_A''$ Two phases, demixing

Phase separation

Consequences $\left. \frac{\partial^2 \Delta G_{mix}}{\partial \phi_A^2} \right|_{\phi_A=0.5} = \frac{1}{\phi_A} + \frac{1}{1-\phi_A} - 2\chi N = 0$ Vanishing curvature

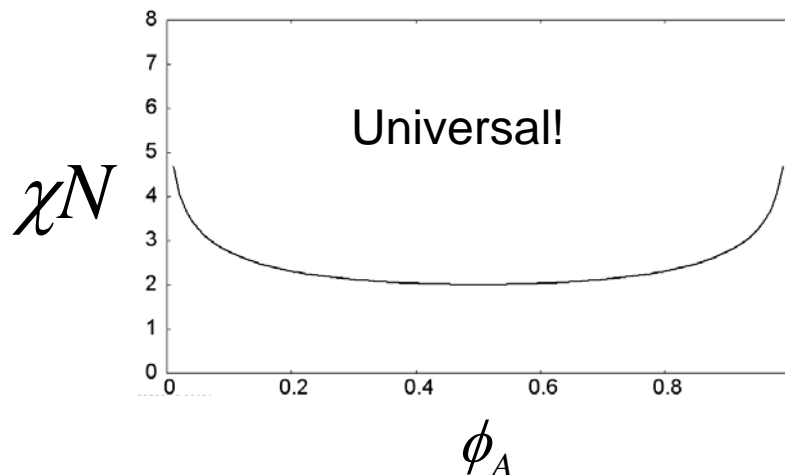
$\chi N = 2$ Critical value: separates region with miscibility gap

$\chi < \chi_c = \frac{2}{N}$ Compatibility through all concentrations, mixing

$\chi > \chi_c$ Miscibility gap $\rightarrow N \gg 0$ $\chi > 0$ No mixing for high molecular weight!

Critical concentrations

$$\frac{\partial \Delta G_{mix}}{\partial \phi_A} = 0$$



Phase separation

In general: upper and lower miscibility gap possible

Include T, one can show (thermodynamics!):

$$\Delta G_{loc} = \Delta H_{mix} - T\Delta S_{loc}$$

\swarrow
 Endo- or exotherm : >0 or <0

$$\chi \sim \frac{1}{T} \quad \chi = \frac{2}{N} \frac{T_c}{T} > 0$$

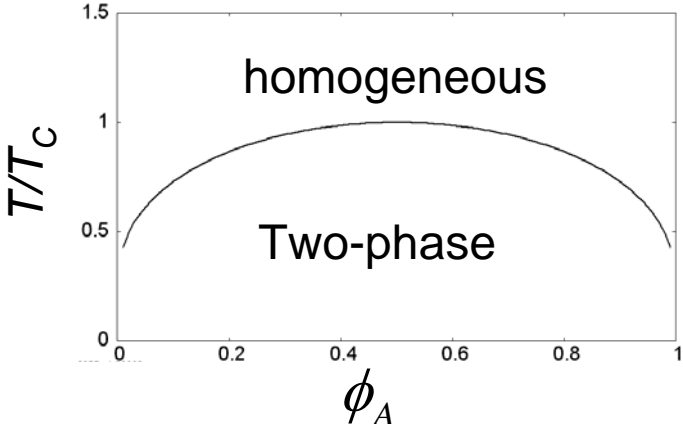
Entropic contributions to ΔG_{loc} (,mobility') neglected

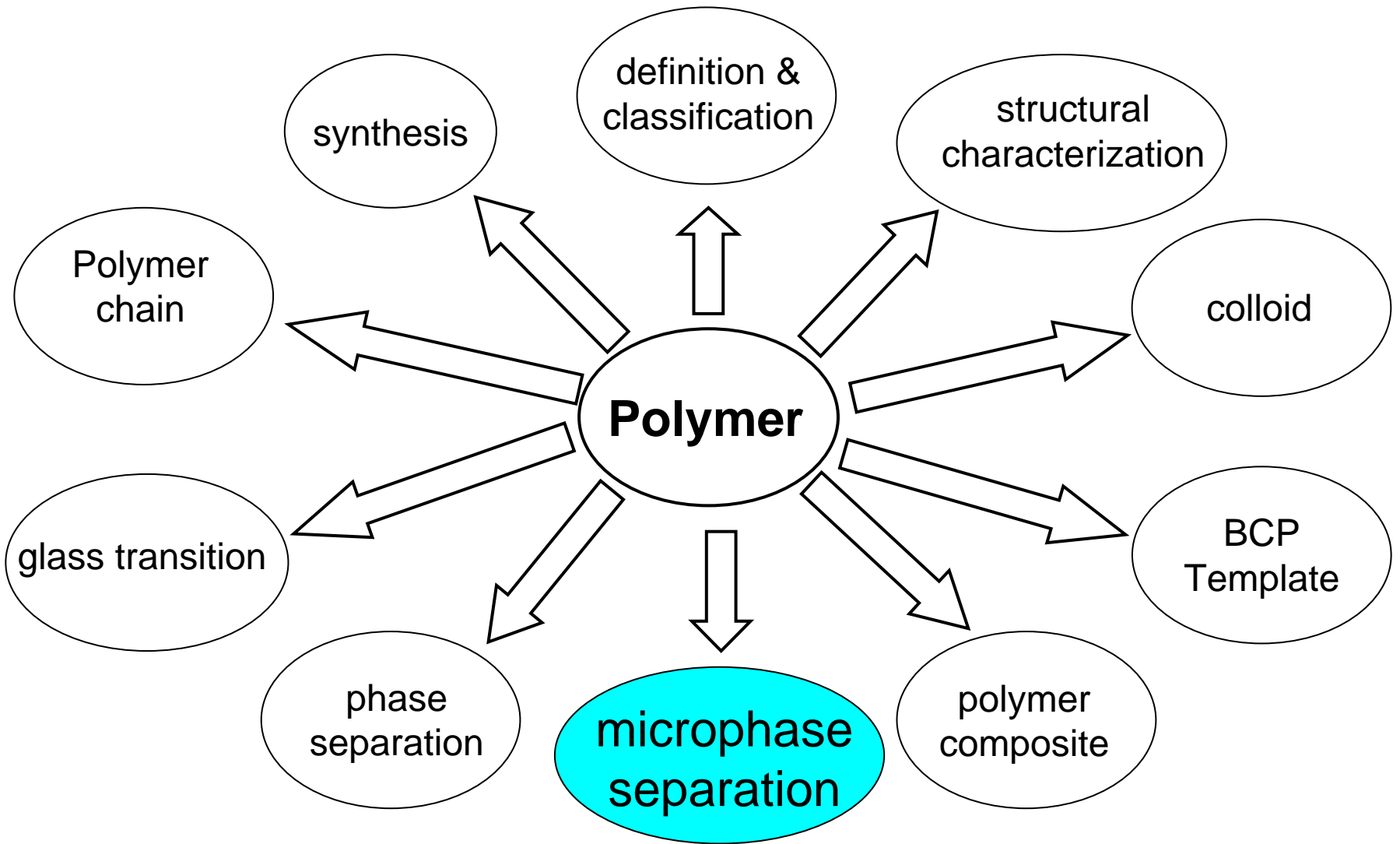
Endothermal polymer mixture

miscibility for high temperatures, if molecular weights low enough

-> mobile enough!

Of course, inverse for exothermal...

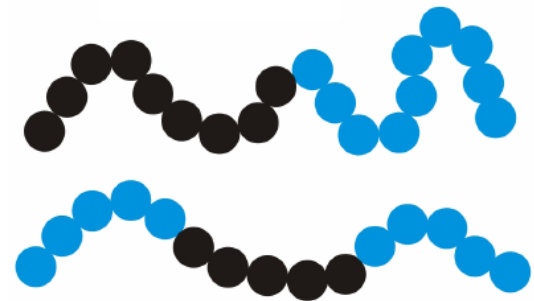




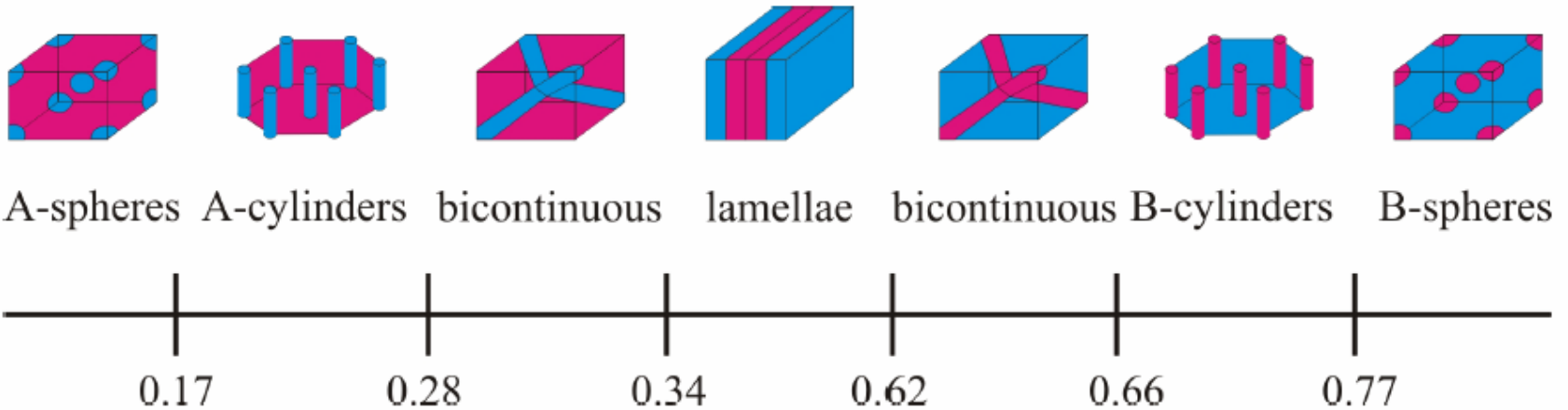
Microphase separation

In a diblock copolymer, where two blocks are built up from two chemically different monomers. Both cannot be separated macroscopically because they are linked by covalent bond, but will segregate with their phase separated domain size having a mesoscopic dimension, which corresponds to the sizes of the single blocks. Because all domains have a uniform size, they can be arranged in a regular manner producing ordered mesoscopic lattices. Such kind of phase separation in block copolymer systems is called **microphase separation**. A theoretical prediction and experimental investigation of microphase separation in block copolymer has been first reviewed by Bates and Fredrickson. The type of the structure depends on the volume fractions of the present blocks. The volume fraction of the block A in an A-B diblock copolymer is determined by:

Volume fraction of block A, $\phi_A = \frac{N_A}{N_A + N_B}$



Microphase separation



Possible mesoscopic lattice structures formed due to microphase separation in block copolymers having blocks of two different types of chemical species assumed as A and B. The numbers given under the boundary of the different structures represent the volume fractions of block A.

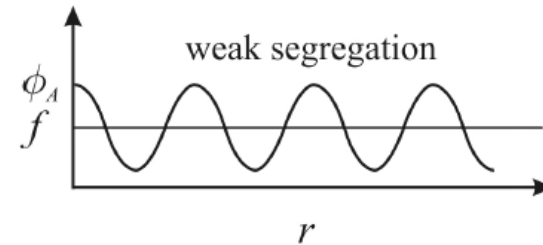
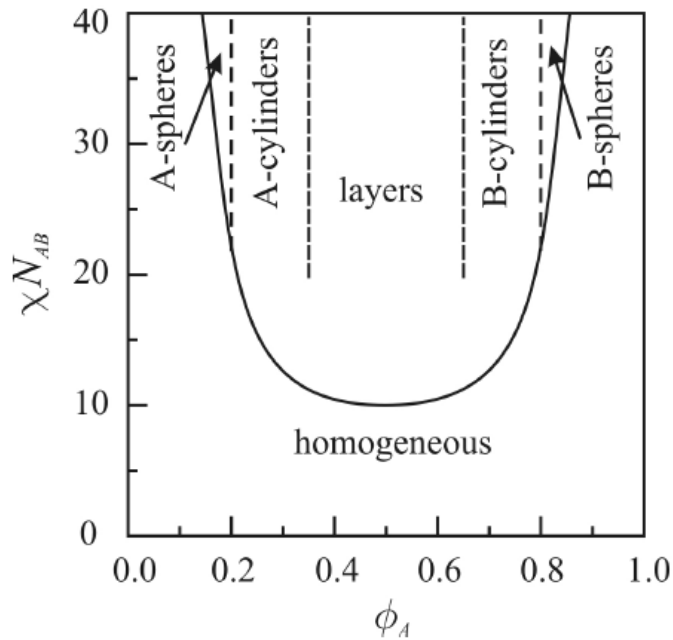
- $N_A \ll N_B \rightarrow$ spherical domains of A in matrix of B will form as body-centered cubic lattice arrangement.
- $N_A < N_B$ ($\phi_A \sim 0.3$) \rightarrow hexagonal array of cylindrical domains of A in matrix of B
- $N_A \approx N_B$ ($\phi_A \sim 0.5$) \rightarrow lamellar arrangement

Microphase separation

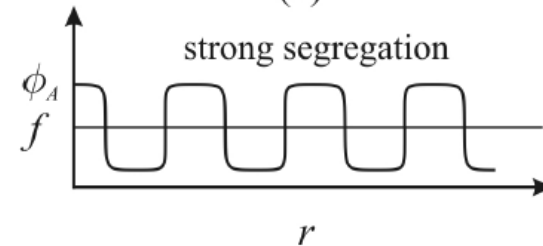
Phase diagram

symmetric block copolymer $(\chi N_A)_c \approx 10.5$

symmetric binary blend $(\chi N_A)_c = 2$

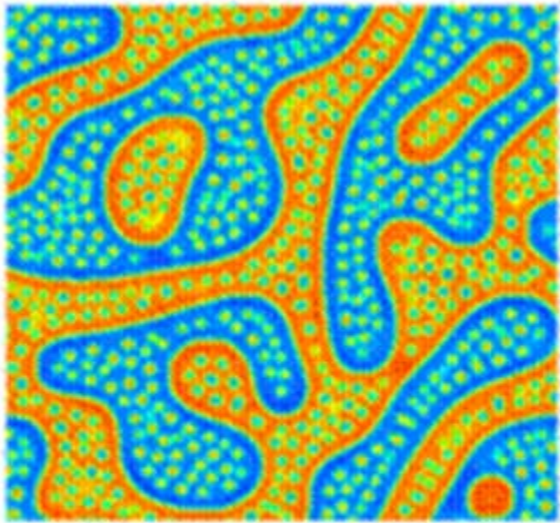


(c)

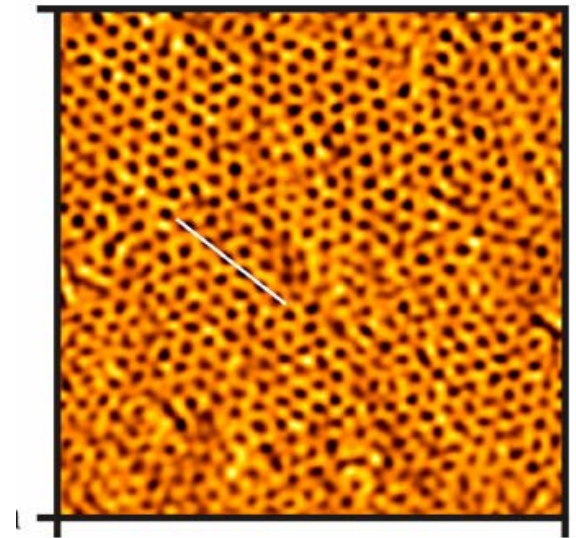
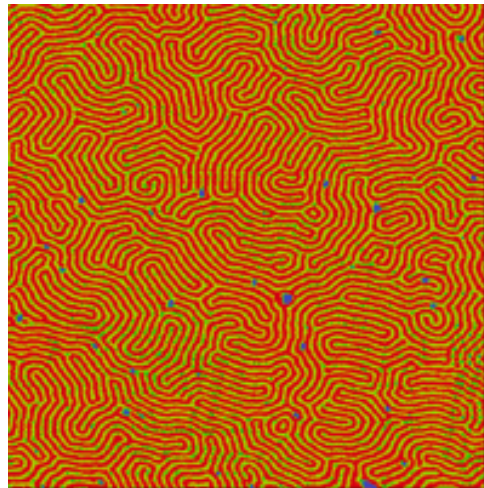


A schematic representation of phase diagram (a) of a diblock copolymer having A and B blocks above the strong segregation limit, $\chi N_{AB} \gg 10$. The solid curve (ODT curve) separates the homogeneous phase and the microphase separated states, where weak segregation occurs. The *dashed boundary lines* represent the boundaries among different types of ordered mesoscopic domain structures. One-dimensional composition profiles of block A in weak (WSL) and strong segregation limits (SSL) are shown in (b) and (c) respectively. ϕ_A and f are the local and stoichiometric (macroscopic) volume fractions of block A, respectively

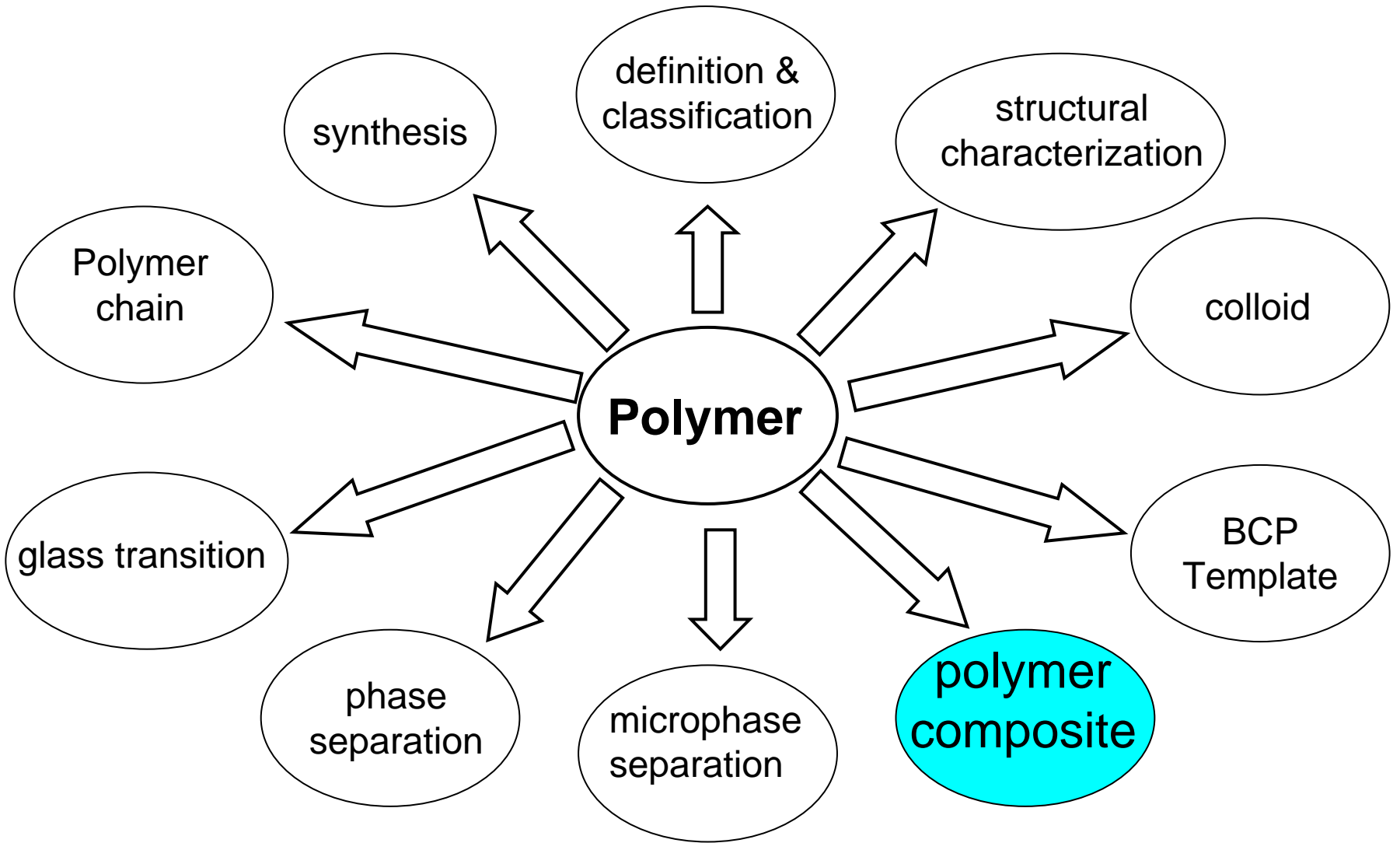
Micrograph of phase separated and microphase separated thin film



A blend of PS/PB



P(S-b-MMA)



Polymer composite

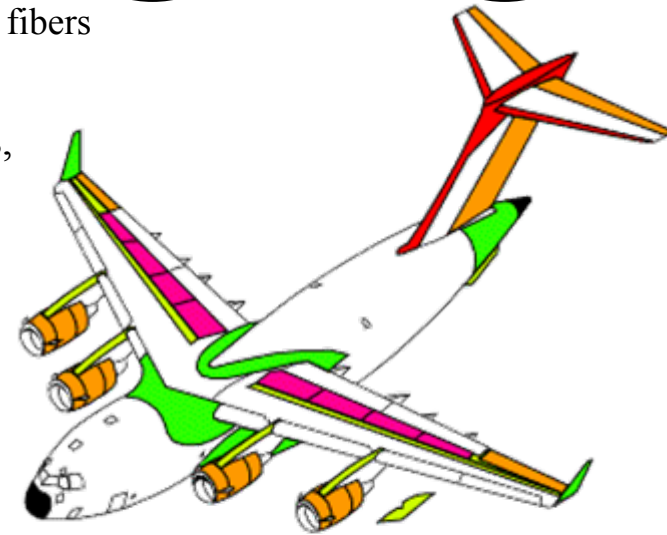
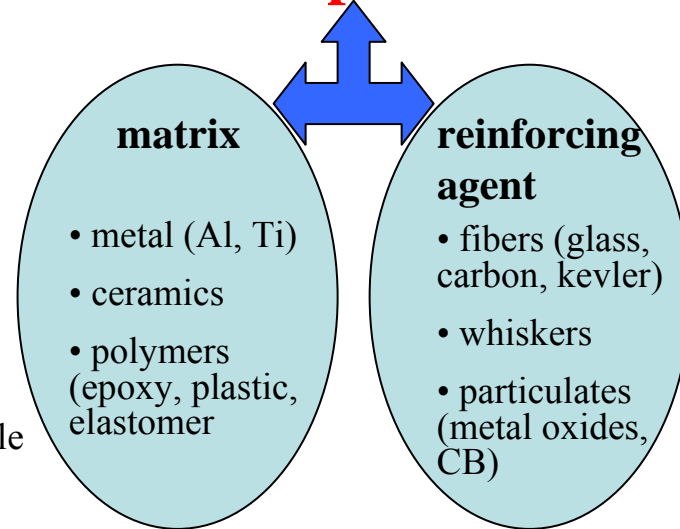


- Throughout history -- ancient building materials, straw/mud huts
- In nature ----- bones in human body are composed of hard brittle hydroxyapatite and soft protein collagen
wood is composed of strong and flexible cellulose fibers surrounded by stiff lignin
- Modern world ----- aerospace, underwater, transportation, sports, commodity life

Why composites?

- Controlled and desired thermal, mechanical, electrical, chemical, optical properties
- low density
- high stiffness
- abrasion and impact resistant
- not easily corroded

composites

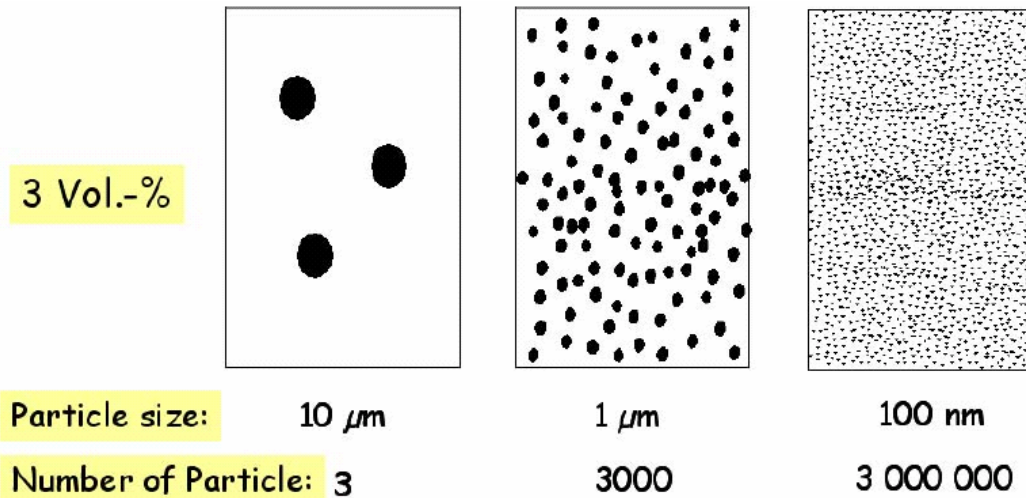


- | | |
|--------------------------------|---------------------|
| Carbon/epoxy | Aramid/DuPont Nomex |
| Carbon/aramid/epoxy | Aramid/foam core |
| Glass-fiber reinforced plastic | Carbon/DuPont Nomex |

Polymer nanocomposites

(at least one dimension of the reinforcing agent is ~ 100 nm or less)

- surface to volume ratio is very high
- property modification at nano-scale
- toughness without sacrificing stiffness
- lighter than metal and other filled composites



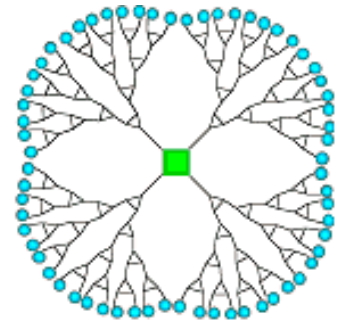
Nanoparticles

(at least one dimension of the particle is ~100 nm or less)

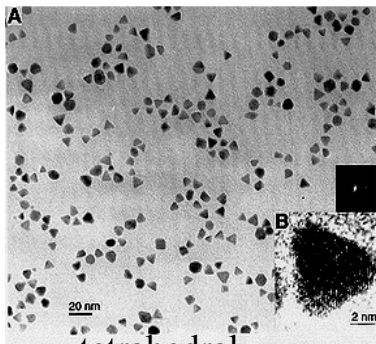
from metal, metal oxide, polymer, hybrid metal oxide and polymer, carbon etc...

Application:

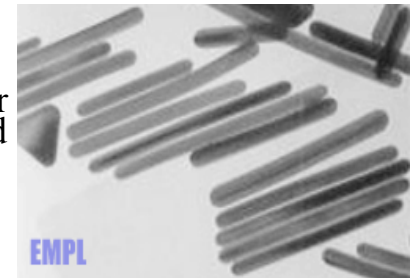
- optical: light based sensor, anti-reflection coating
- magnetic: increased storage density media, MRI
- mechanical: composites----wear resistance, anti-corrosion, stronger and lighter
- electronic: capacitor in mobile phone, displays, high conductivity materials
- biomedical: antibacterial coating on wounds dressings, sensor for diseases, drug delivery, “interactive” food and beverages
- environmental: clean up of soil contamination and pollution, e.g. oil, biodegradable polymers, aids for germination. treatment of industrial emissions.



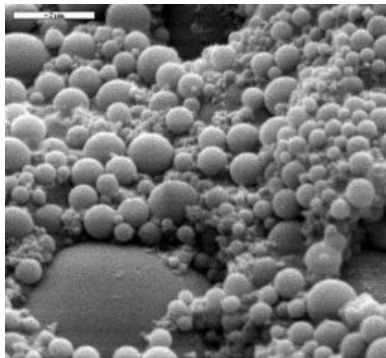
dendrimeric



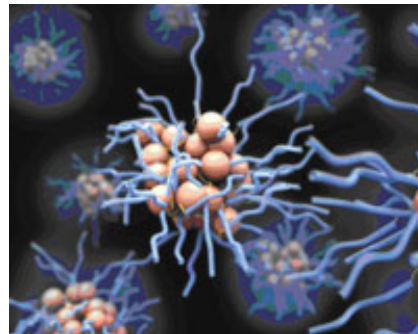
tetrahedral



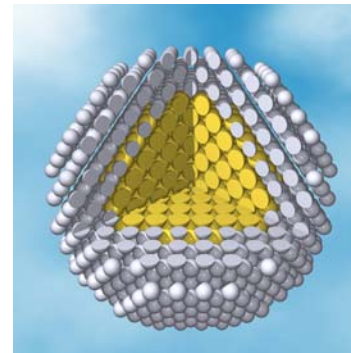
gold nanorod



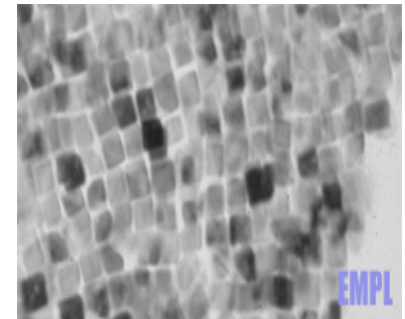
SiO₂



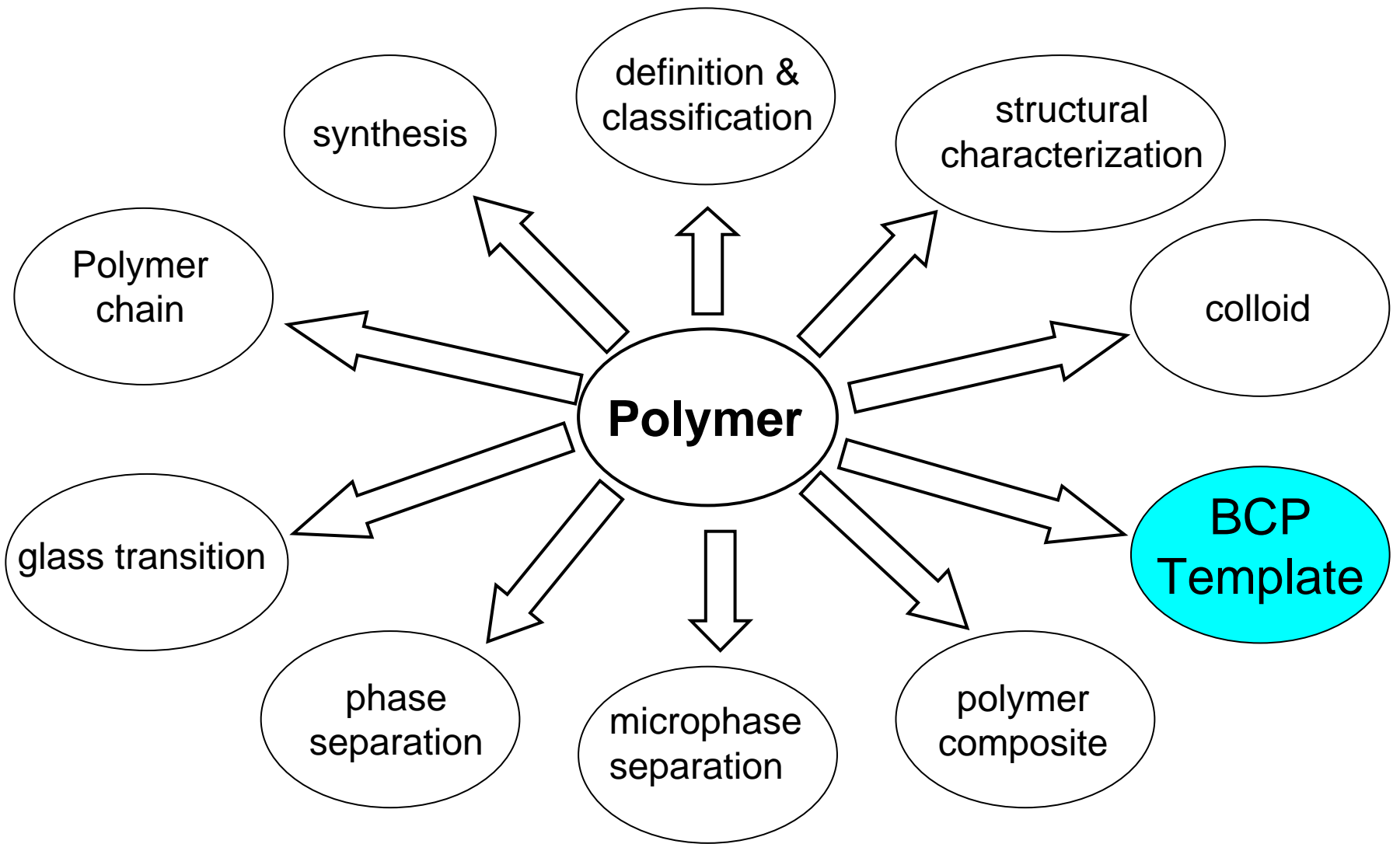
polypeptide



core-shell

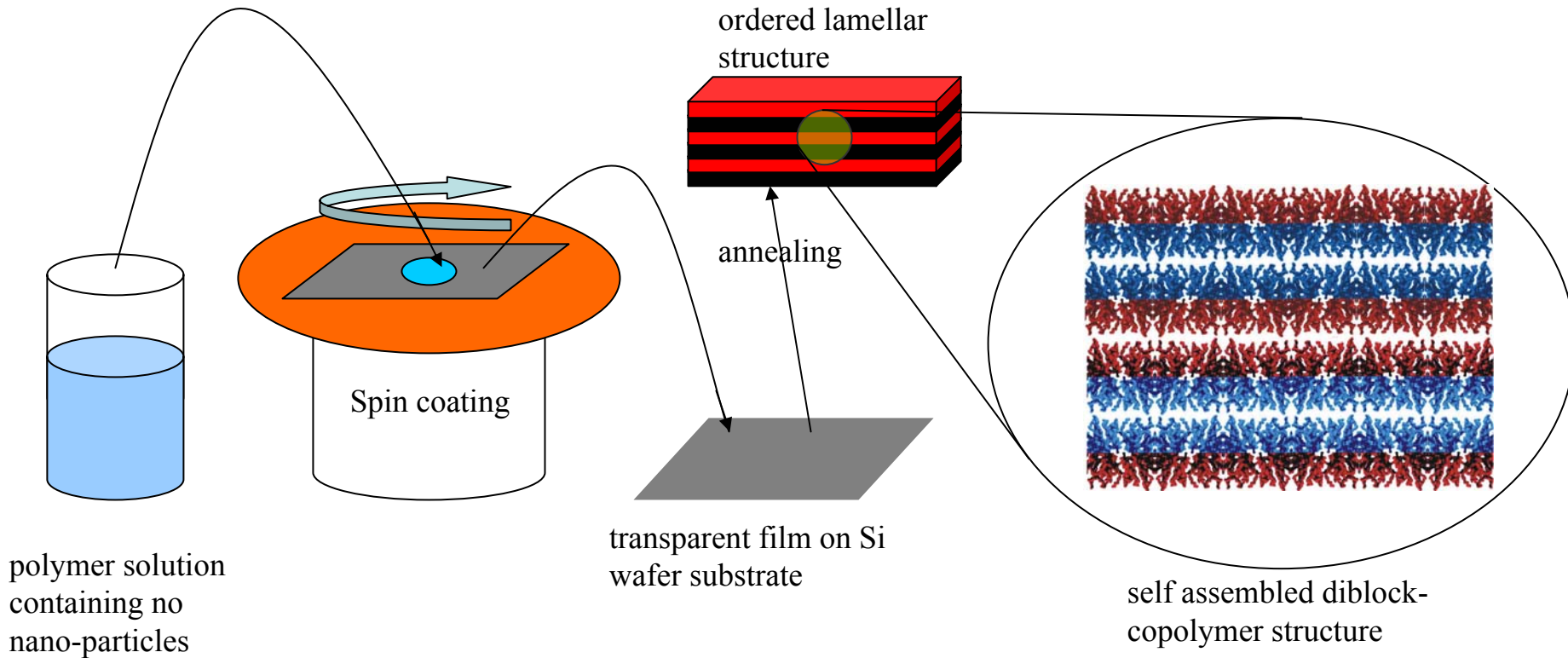


cubic titania



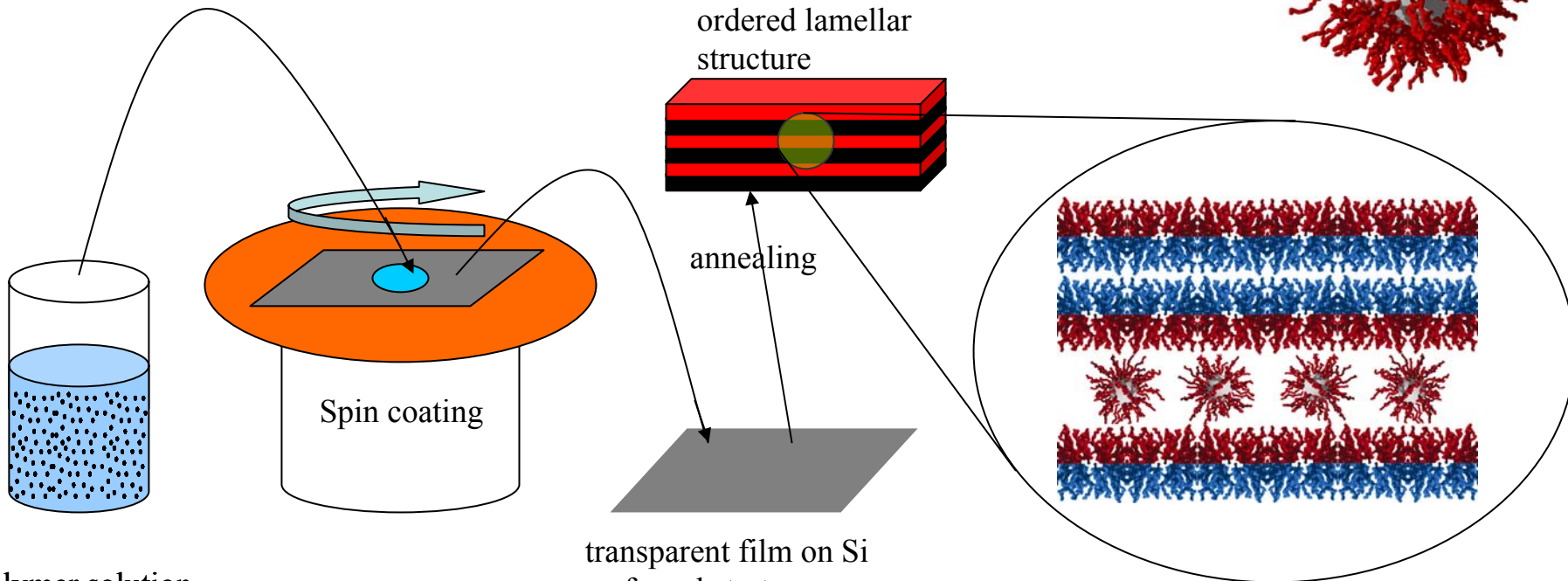
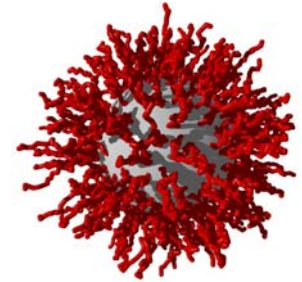
Block copolymer template

template offered by block copolymer
nano-structures



Block copolymer template

template offered by block copolymer nano-structures + hairy magnetic nanoparticles

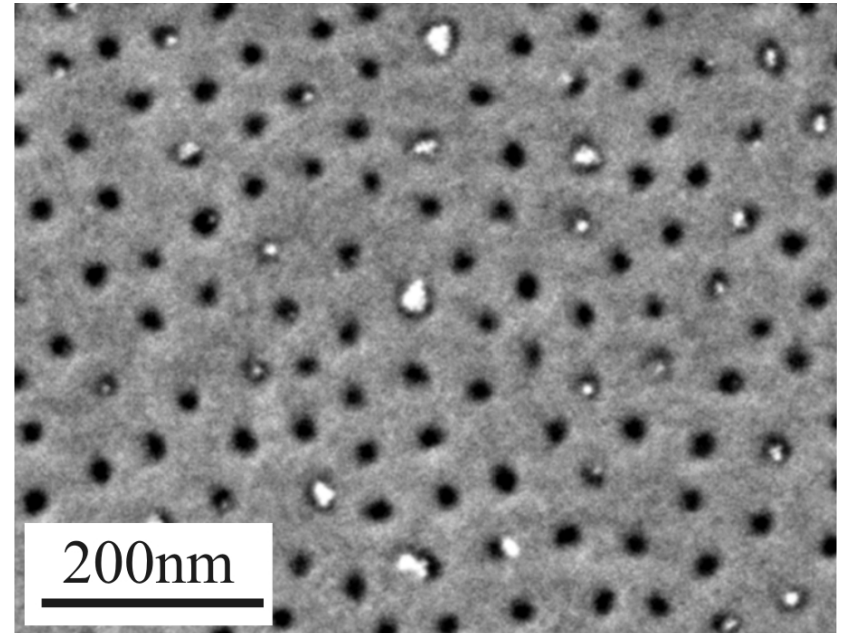
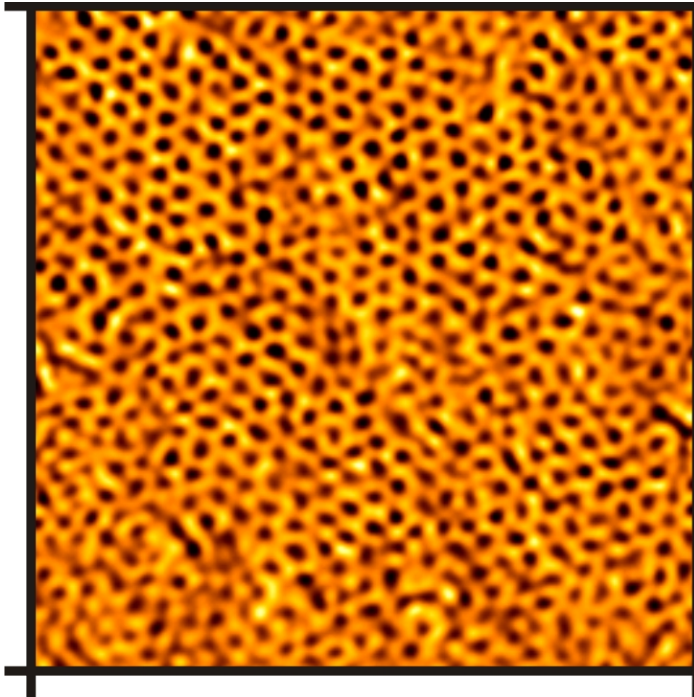


polymer solution containing nanoparticles

transparent film on Si wafer substrate

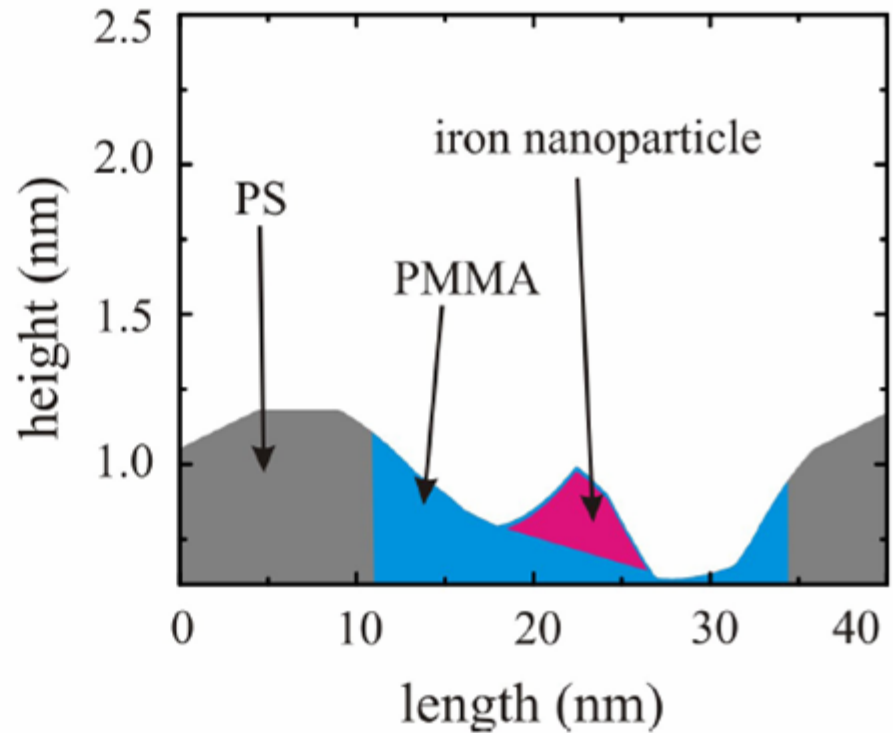
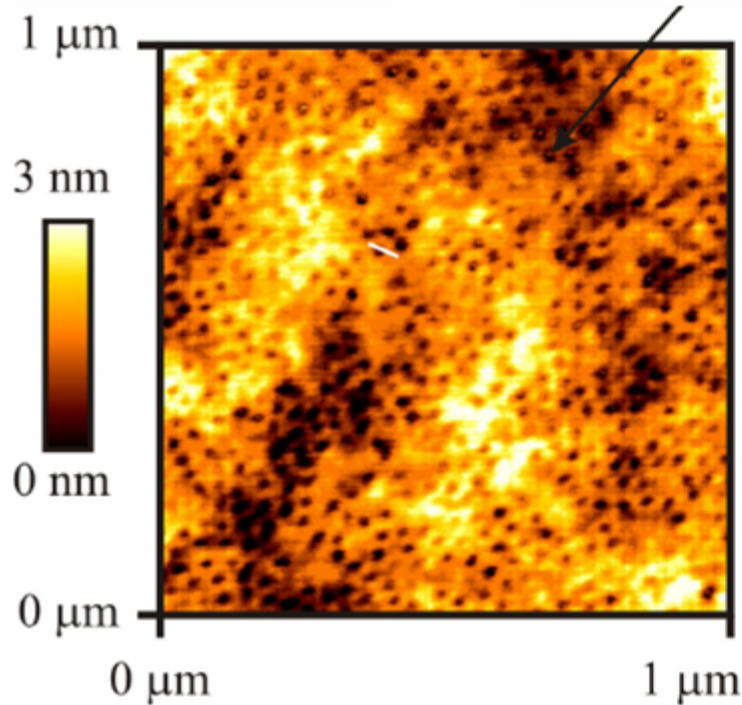
nanoparticles distribution inside the layers due to selective affinity to one block

Block copolymer template



Particle cooperative self assembly / directed self assembly

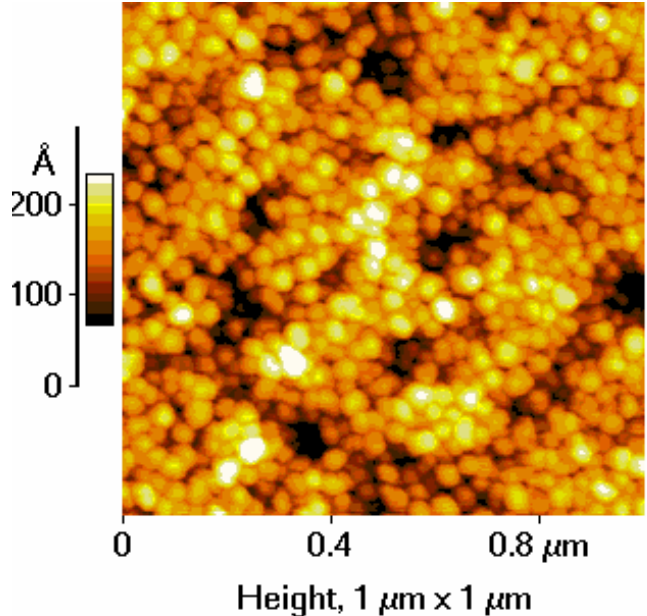
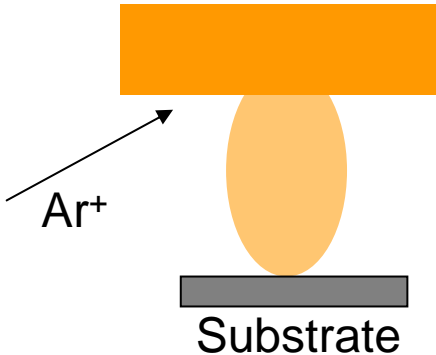
Block copolymer template



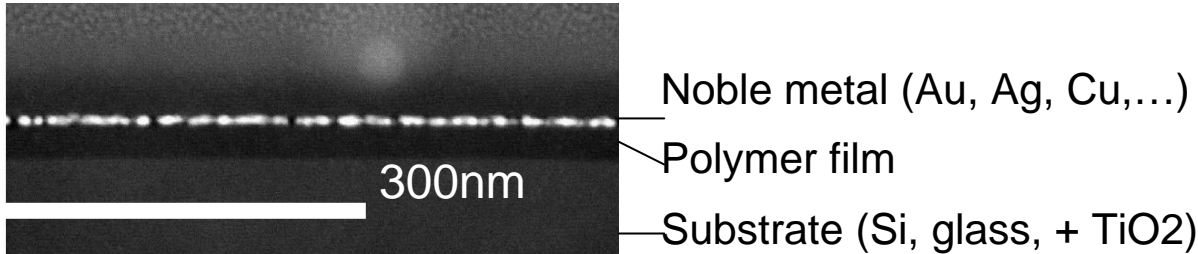
Sputter deposition of iron atoms

Polymer-Metal Nanocomposites: Production

Sputter deposition:



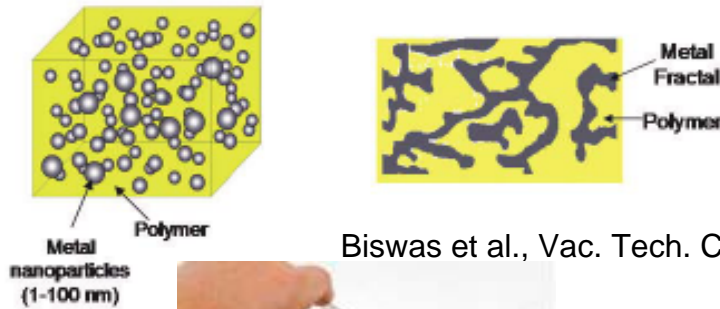
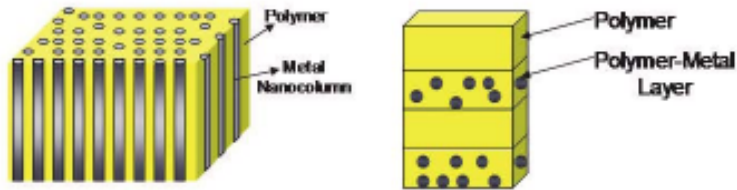
- Nice clusters, too
- Fast deposition method
- Usually broader size distribution
- self-assembly: Au-Au interaction much stronger than Au-Polymer interaction



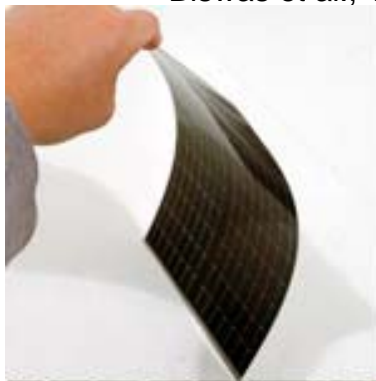
Roth et al., Appl. Phys. Lett. **88**, 021910 (2006)

Block copolymer template

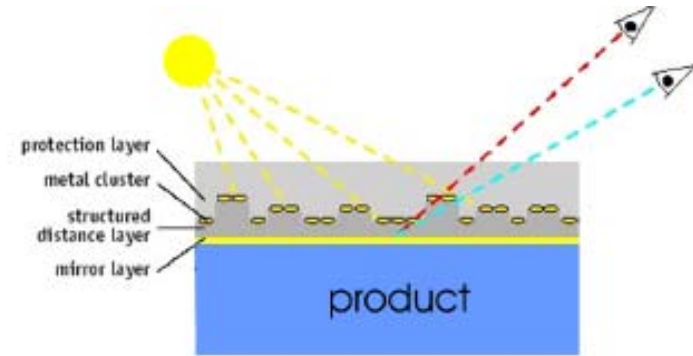
Polymer-Metal Nanocomposites



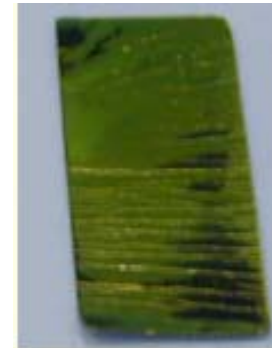
Biswas et al., Vac. Tech. Coat. 7, 54 (2006).



<http://www.siliconsolar.com>



Bauer et al., Nanotechnology 14,1289 (2003)



14°

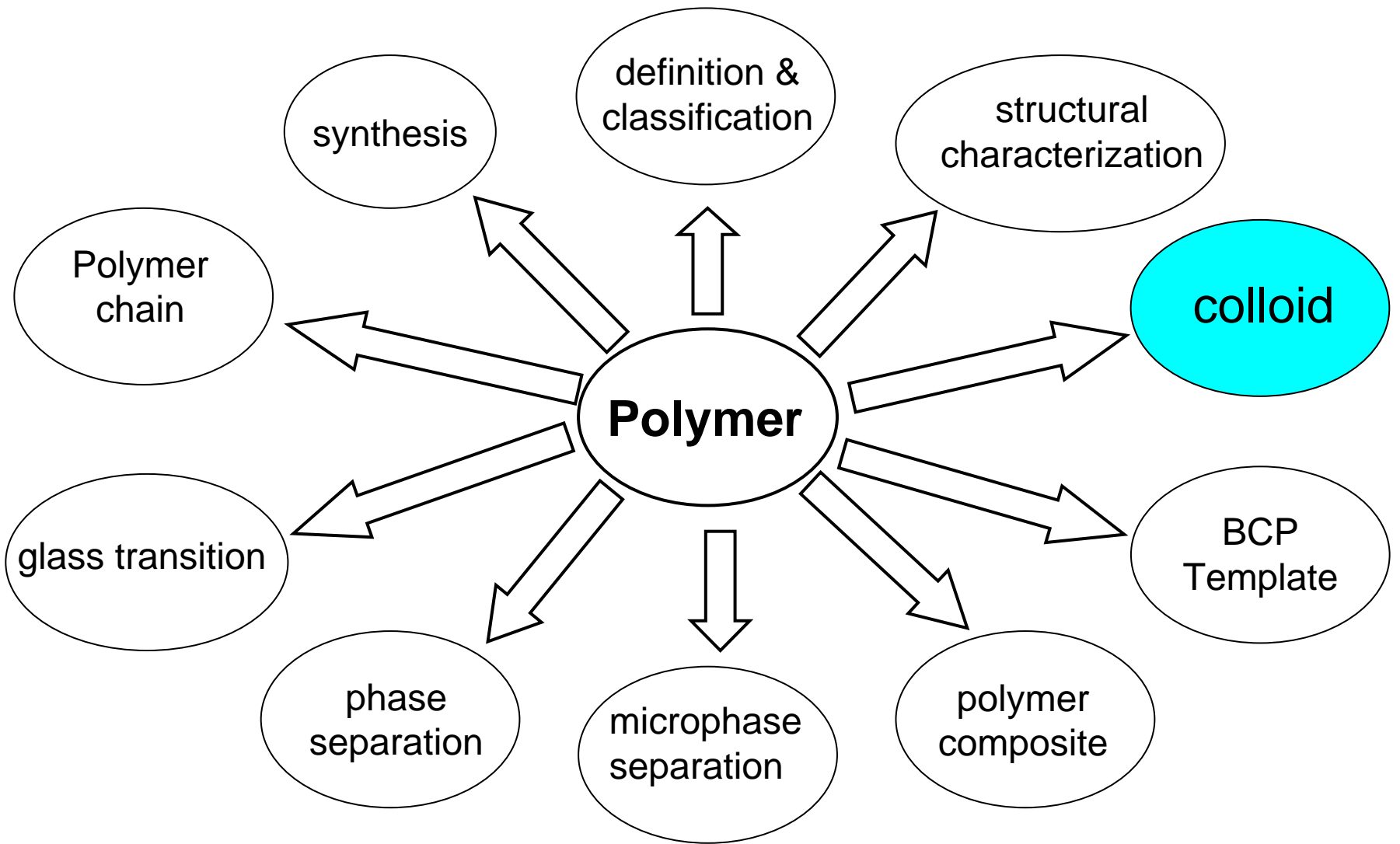


90°

**High-frequency filters
Solar cells**

$$v_{lim} \sim \rho/R^2$$

**Anti-counterfeiting
Biosensors**



Colloids

A **colloid** is a type of mixture of two separate phases: a *dispersed phase* (or *internal phase*) and a *continuous phase* (or *dispersion medium*). A colloidal system may be solid, liquid or gas.

- Polymers
- Metals

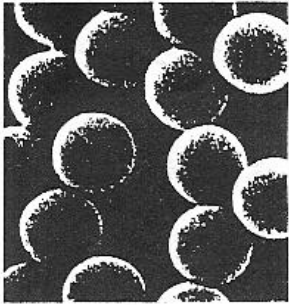
- Small particles, dispersed in liquid phase
- Size: nm.... μm
- Wall paints, milk
- Polymers: Spheres



Emulsion polymerization: Example latex particles (styrene/butadiene)

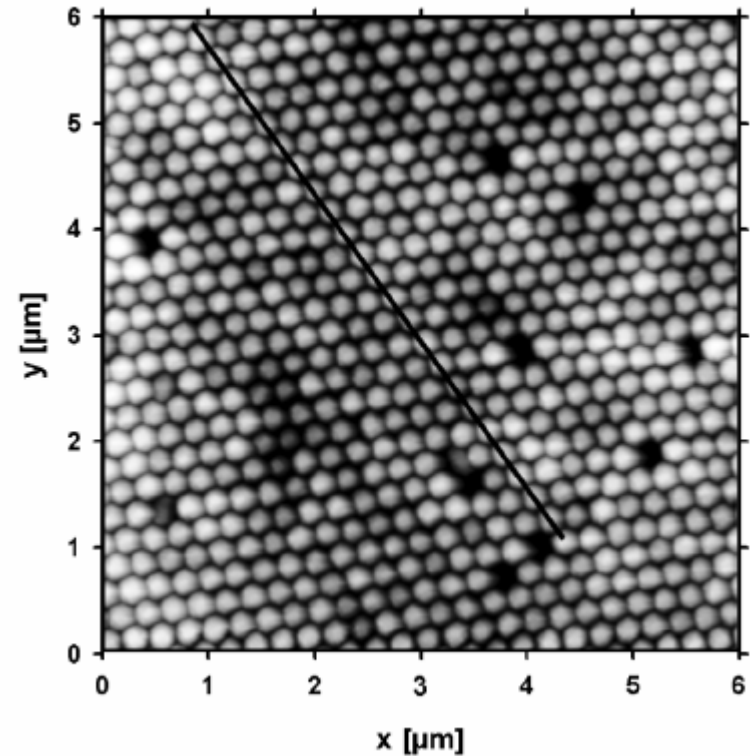
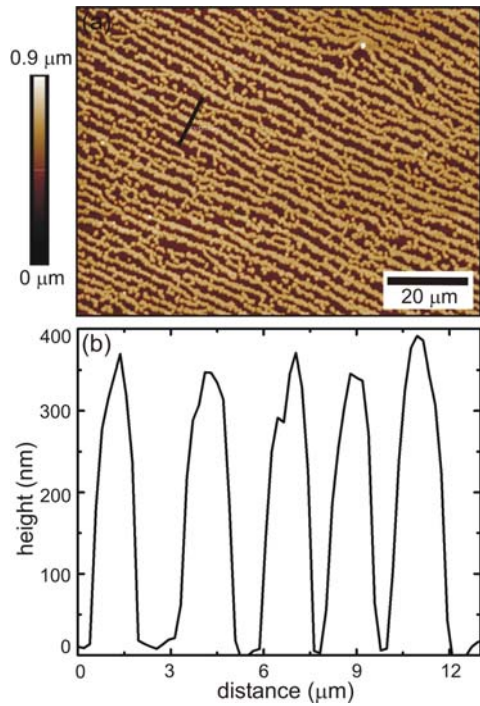
Polymer colloids

... and you obtain nice spheres:



[Springer]

... which you can nicely arrange here in 2D:

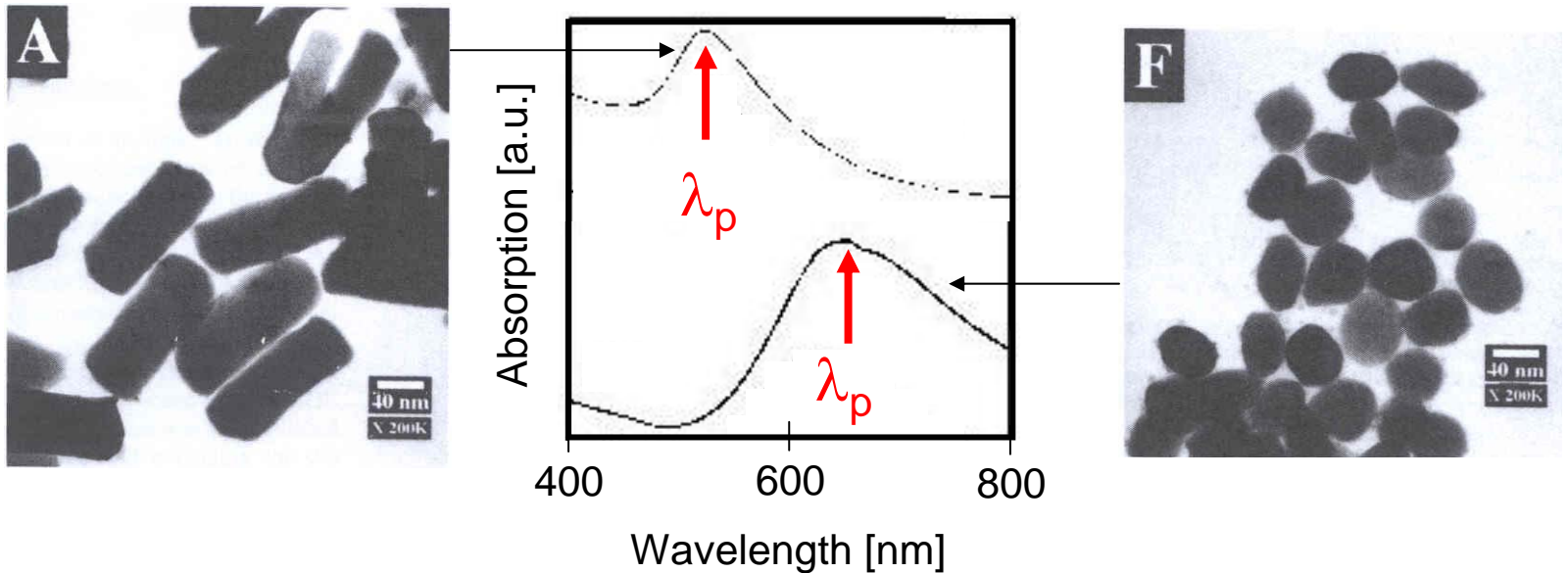


[Frömsdorf, J. Chem. Phys. (2006)]

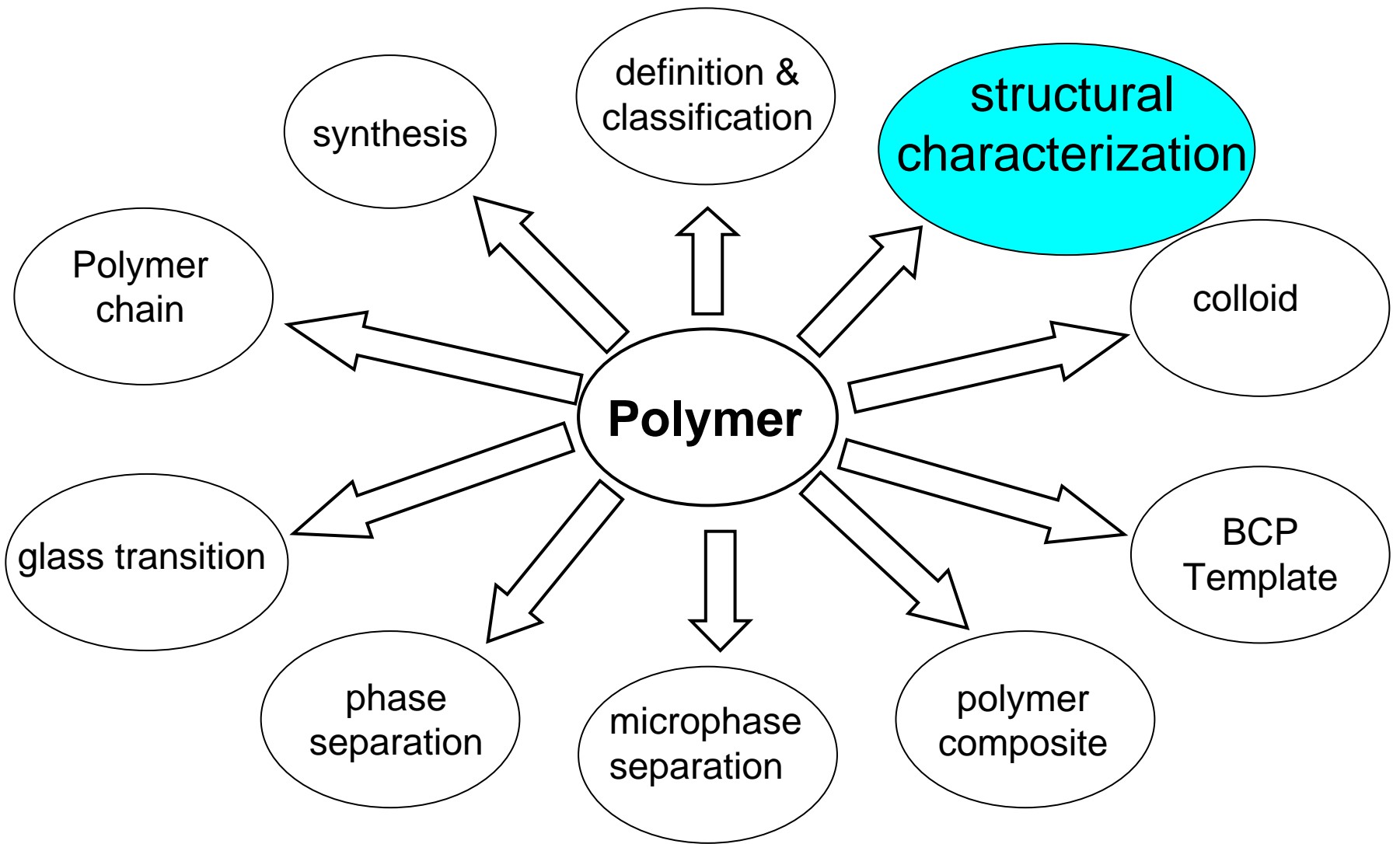
Colloids

Application

Optical properties: sharp resonances (visible light) \leftrightarrow plasmon resonances cluster arrangement & shape



J.C. Hulteen et al., J Phys. Chem. B 101, 7727 (1997)



Structural Characterization

1. Optical microscopy (OM)
2. Atomic force microscopy (AFM)
3. Scanning electron microscopy (SEM)
4. Transmission electron microscopy (TEM)
5. Small-angle X-ray scattering (SAXS)
6. Ultra small-angle X-ray scattering (USAXS)
7. Grazing incidence small-angle X-ray scattering (GISAXS)
8. Grazing incidence ultra small-angle X-ray scattering (GIUSAXS)
9. Wide-angle X-ray scattering (WAXS)
10. X-ray reflectivity (XRR)
11. Dynamic light scattering (DLS)
12. Ellipsometry