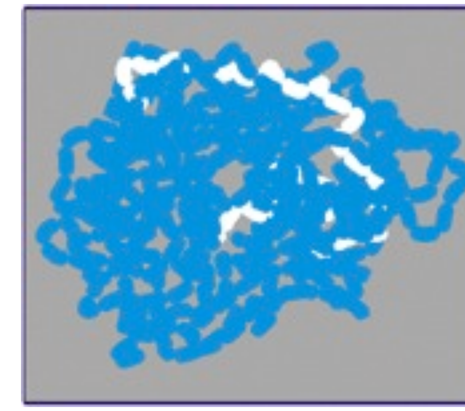
Polymers: from plastic bags to advanced functional nanomaterials

Reidar Lund

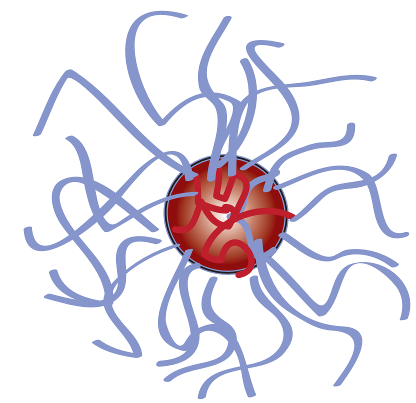
Dept. of Chemistry (Ø 207, Kjemibygningen)
University of Oslo
Email: reidar.lund@kjemi.uio.no

Outlook



- What is a **polymer** ?

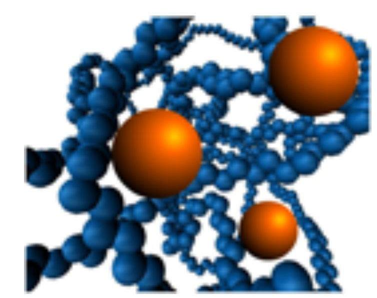
- What **special properties** do polymer materials possess?

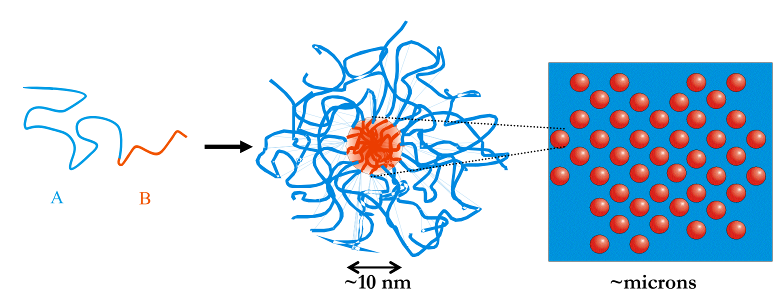


- **Nanostructures** with polymers: **self-assembly**

- **Nanocomposites**: combining the best from the inorganic and organic world

- **Drug delivery**: nano-vehicles to the cell

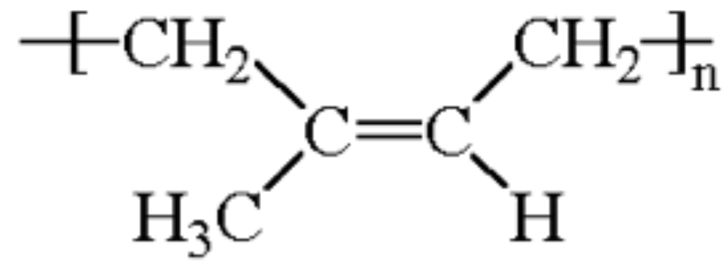




Polymers

chain-like molecules

Example: polyisoprene (natural rubber)



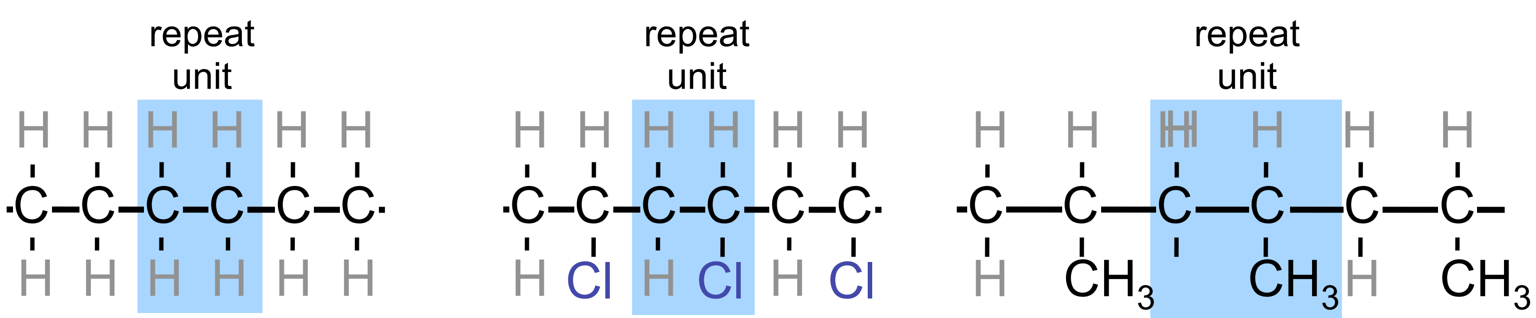
What is a polymer?

What is a polymer?

Chain-like molecules

Poly **mer**

many **repeat unit**

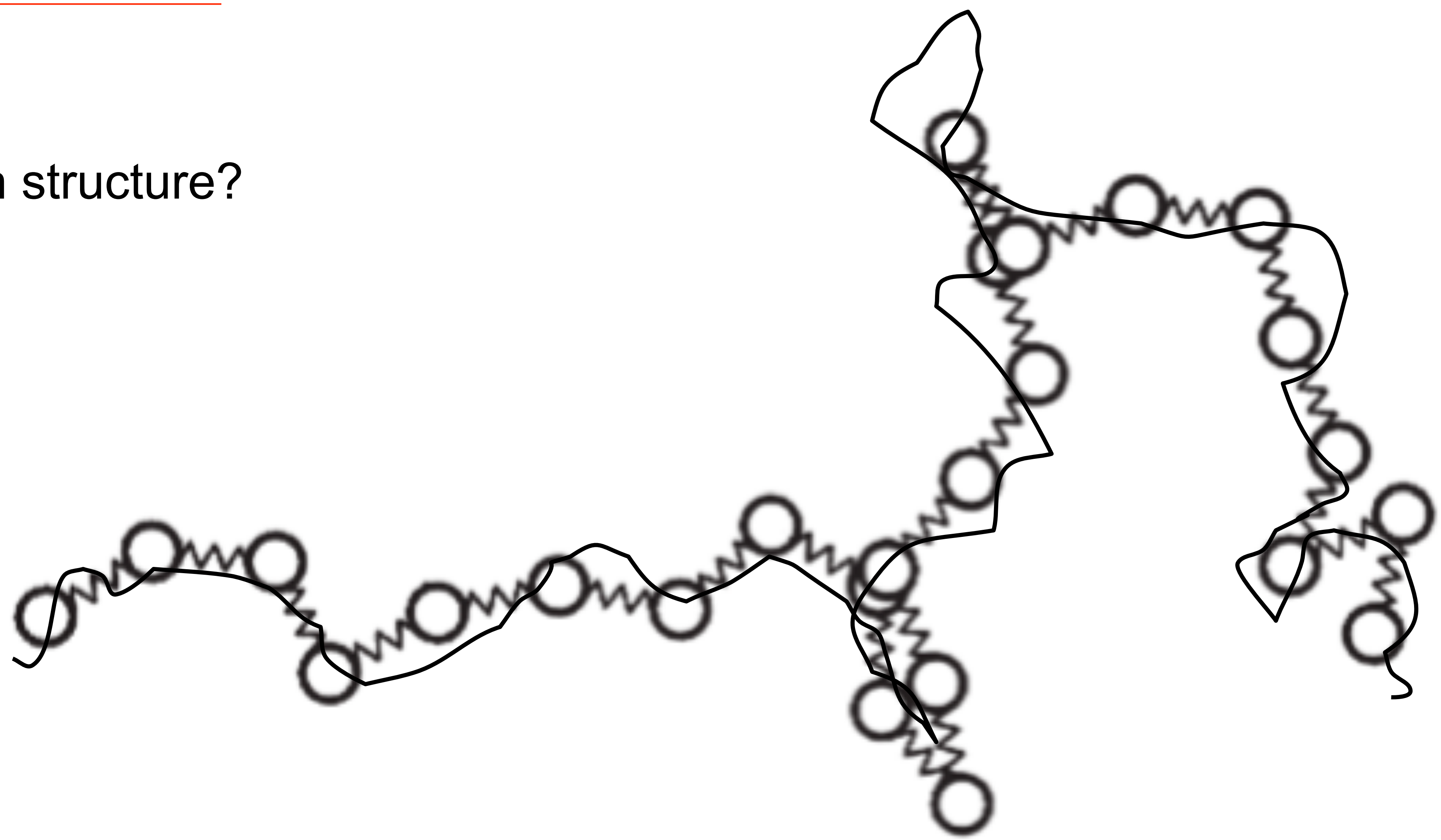


Polyethylene (PE) Polyvinyl chloride (PVC) Polypropylene (PP)

But how do they look like?

How does a polymer chain look like?

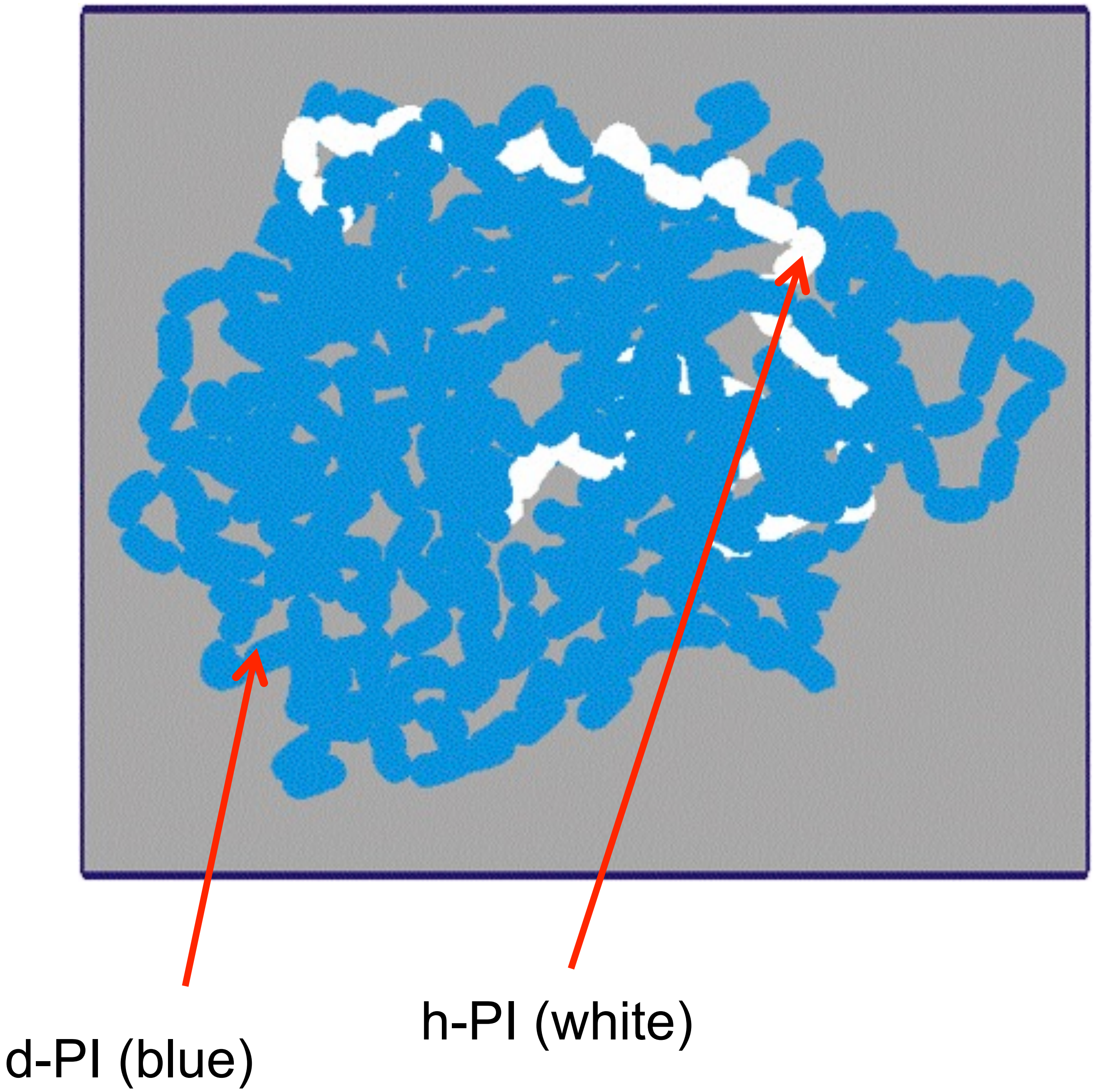
Model:
random chain structure?



Rouse 1953
Flory: nobel prize 1974

We can see a single polymer chain with neutron scattering

Neutrons see deuterium (H^2/D) and hydrogen (H^1) very differently

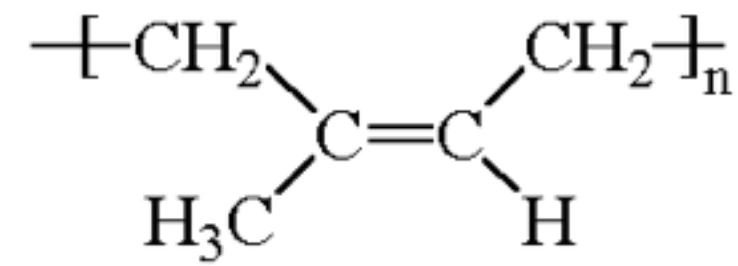


Small-angle Neutron Scattering (SANS) at IFE, Kjeller

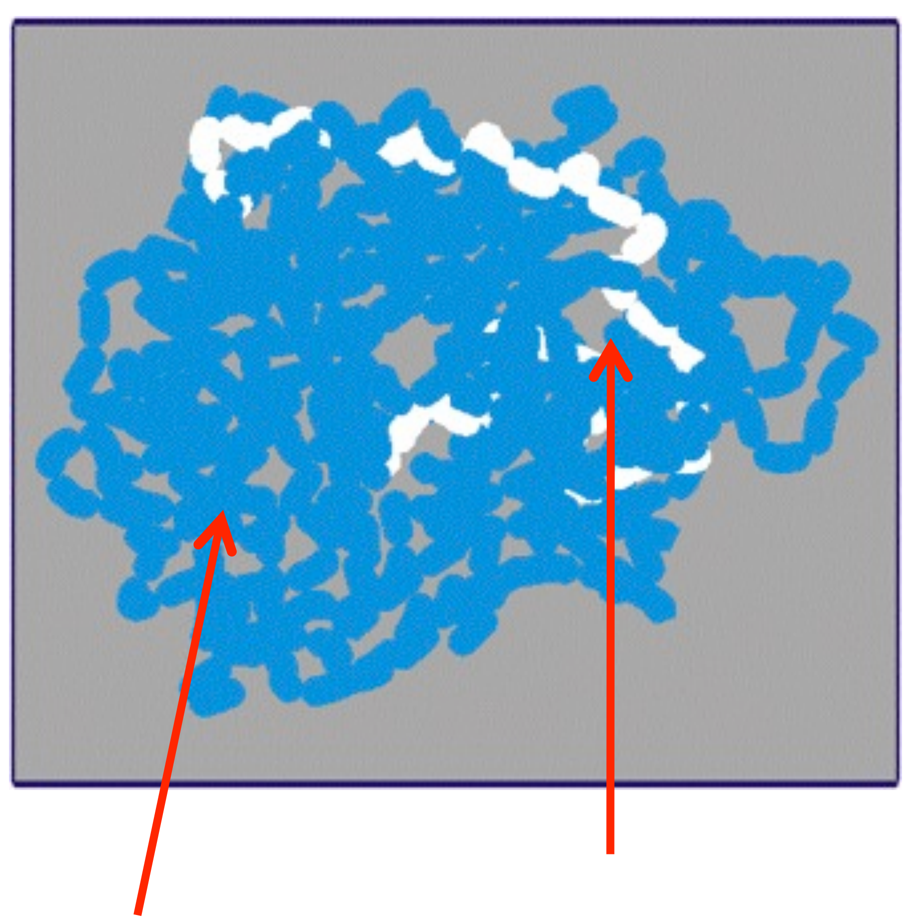
Institut Laue Langevin (ILL), Grenoble (France)

Conformation of single polymers with SANS

Example: polyisoprene

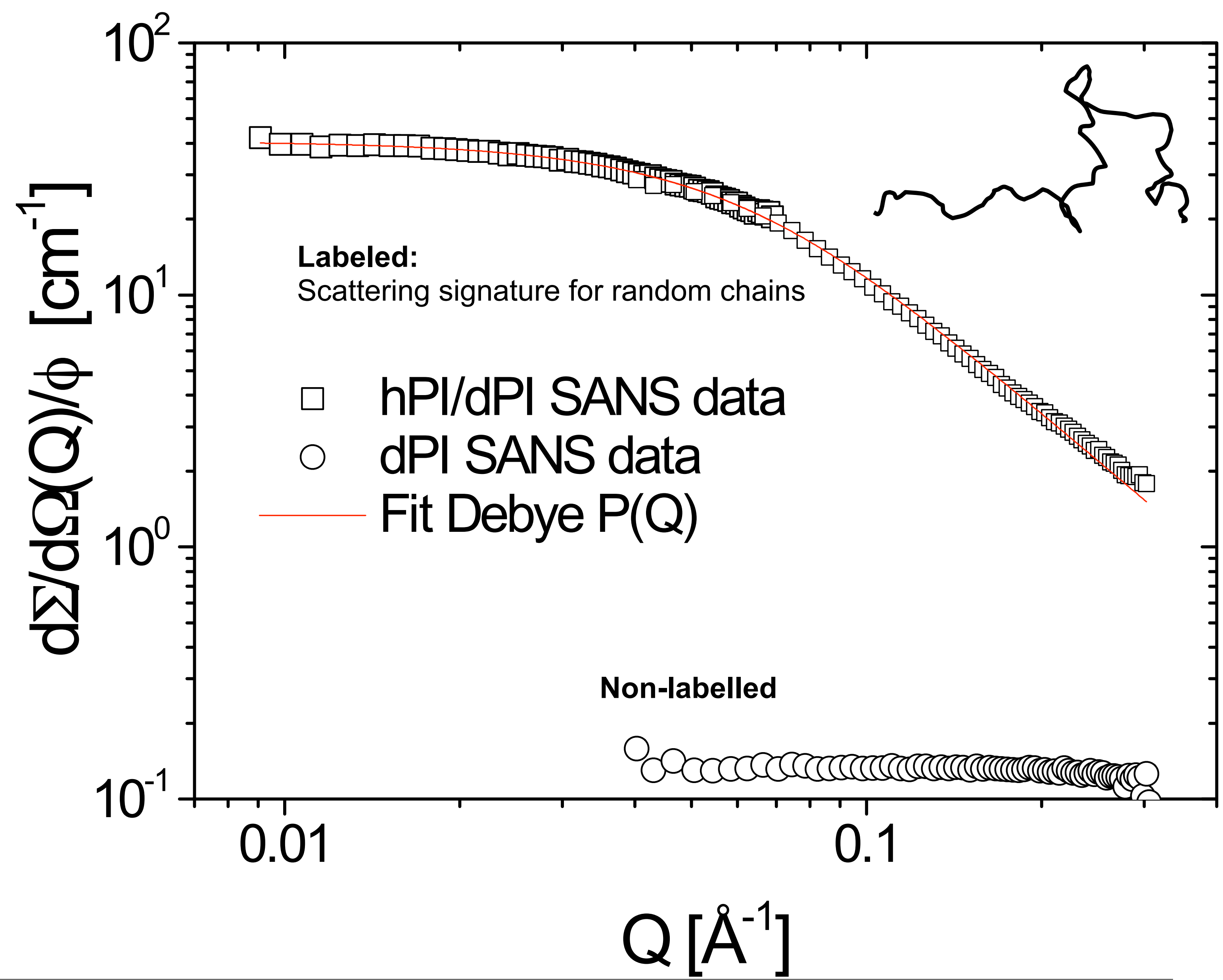


Neutrons see deuterium and hydrogen very differently



d-PI (blue)

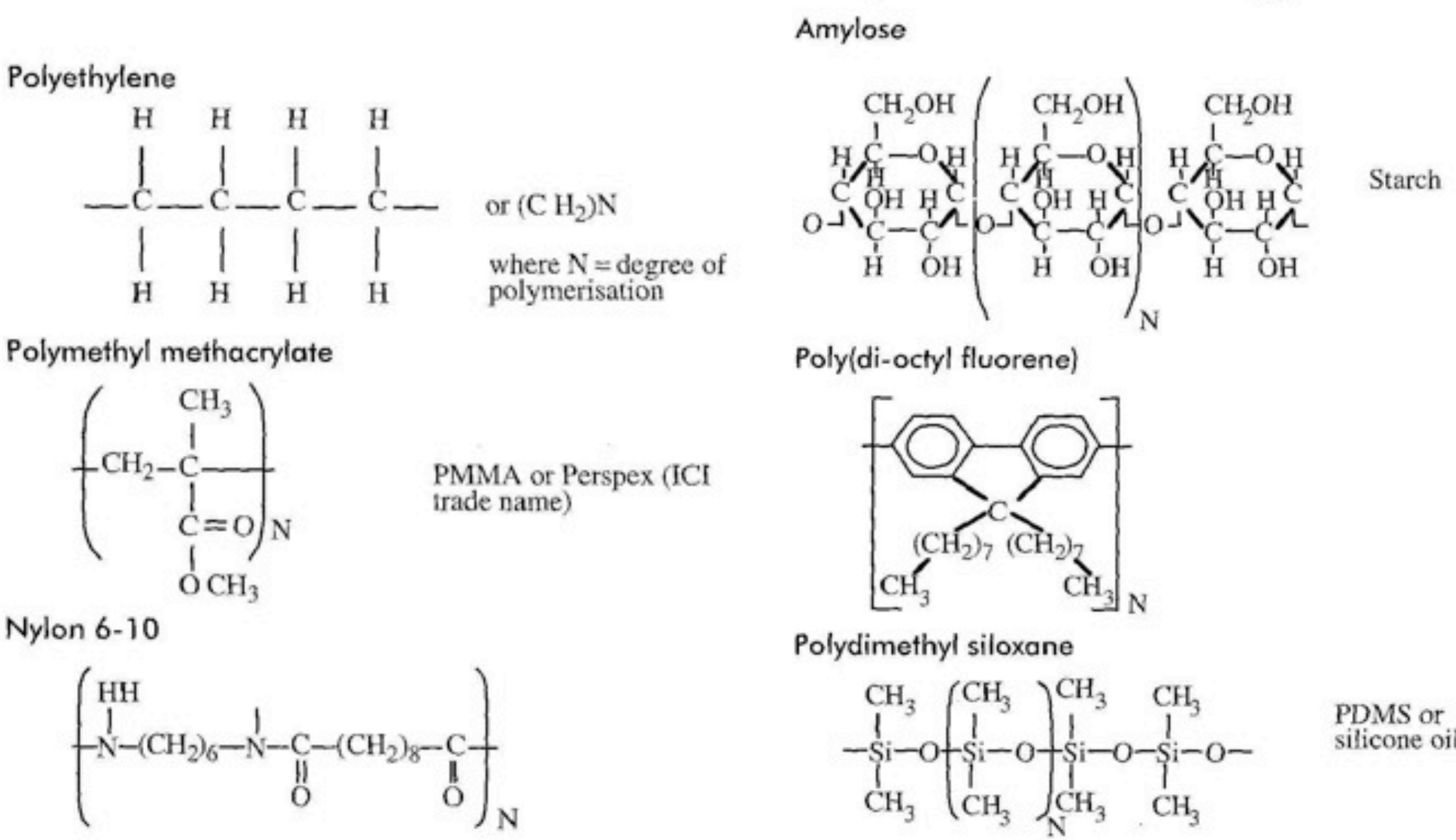
h-PI (white)



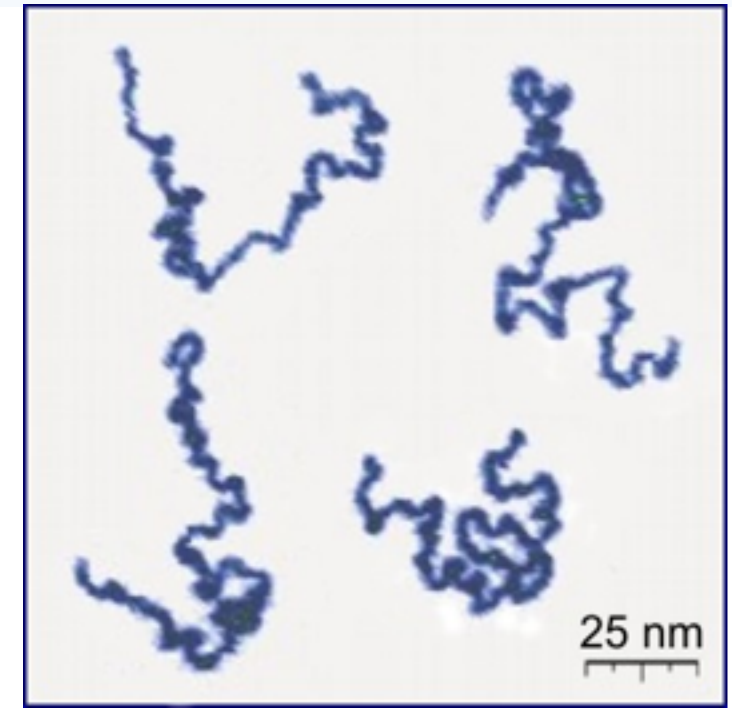
Answer: random (Gaussian) chain in a «soup of spaghetti»

Polymers: example

Chain-like molecules



single polymers



many polymers: «spaghetti»

In general: polymers are *long molecules* (varying stiffness)

Classical applications of polymers

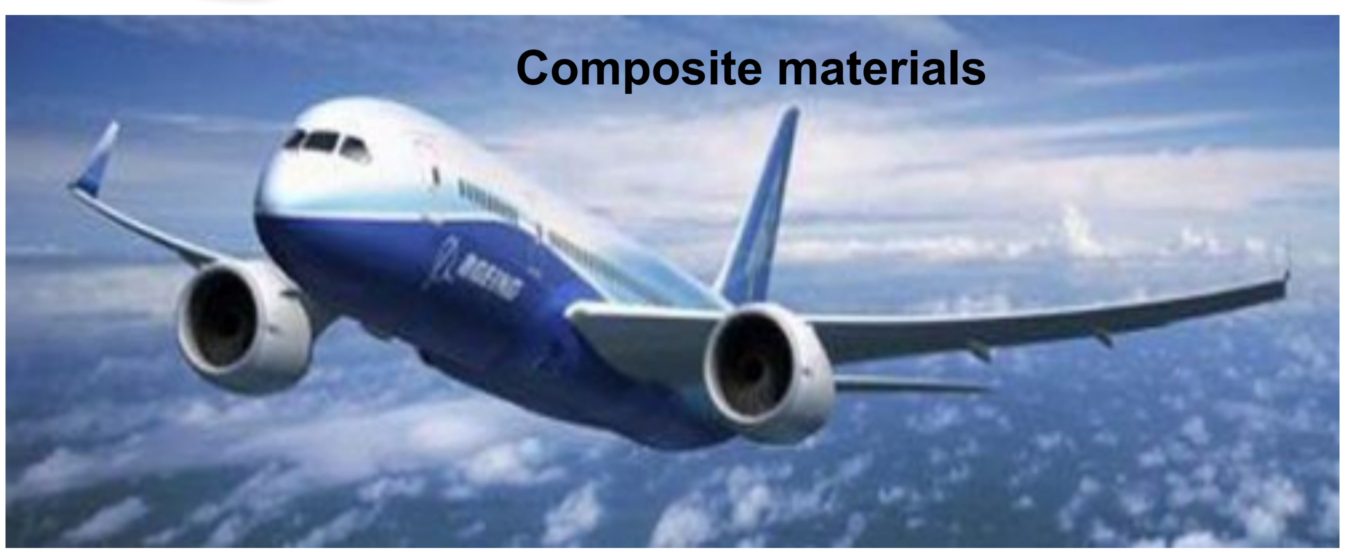
PI rubber

PP for food wrapping

PVA as diapers

PTFE (Teflon) coatings

PET bottles



Composite materials

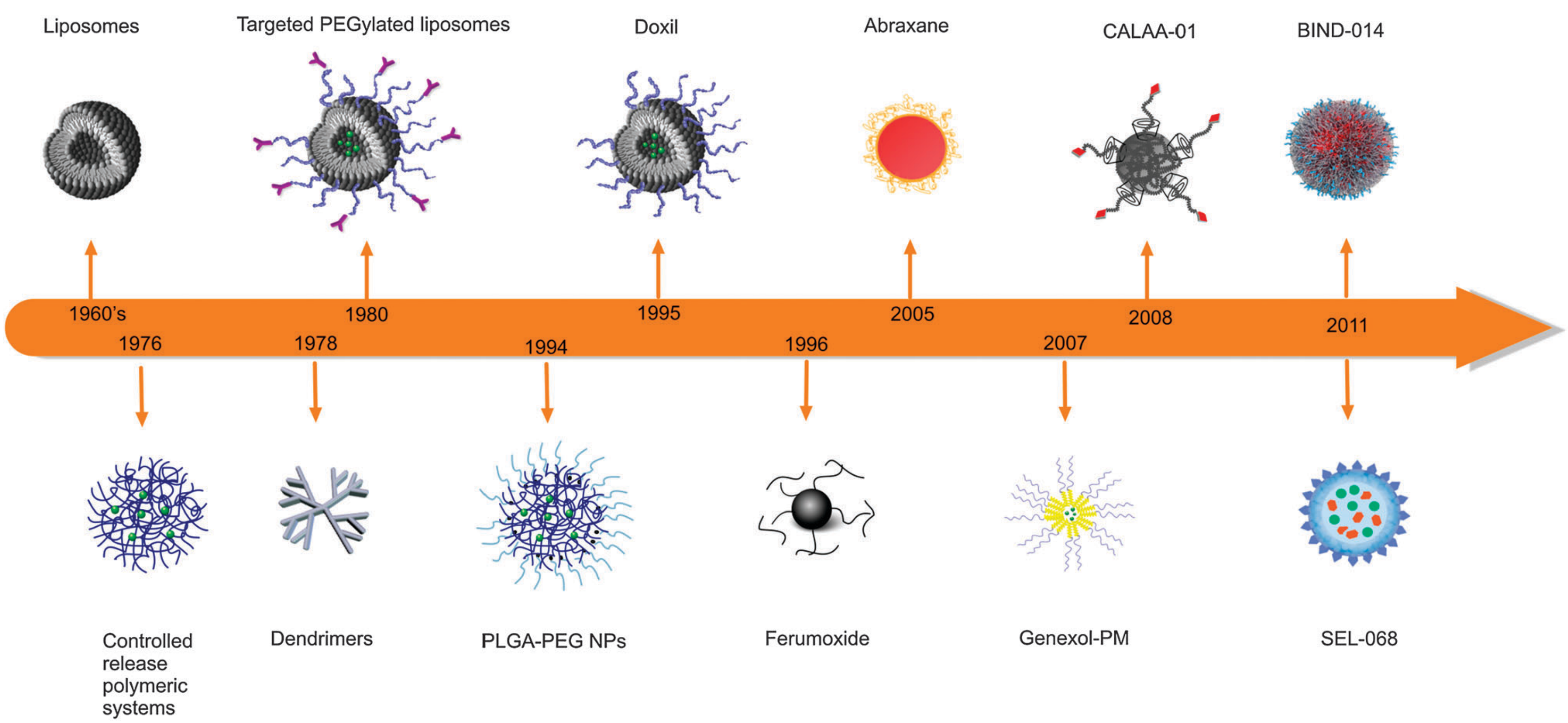
Boeing Dreamliner 787: 50% composite, 20% aluminum, 15%titanium, 10% steel, 5% other.

Bullet-proof vest: Kevlar

Semi-conductor industry

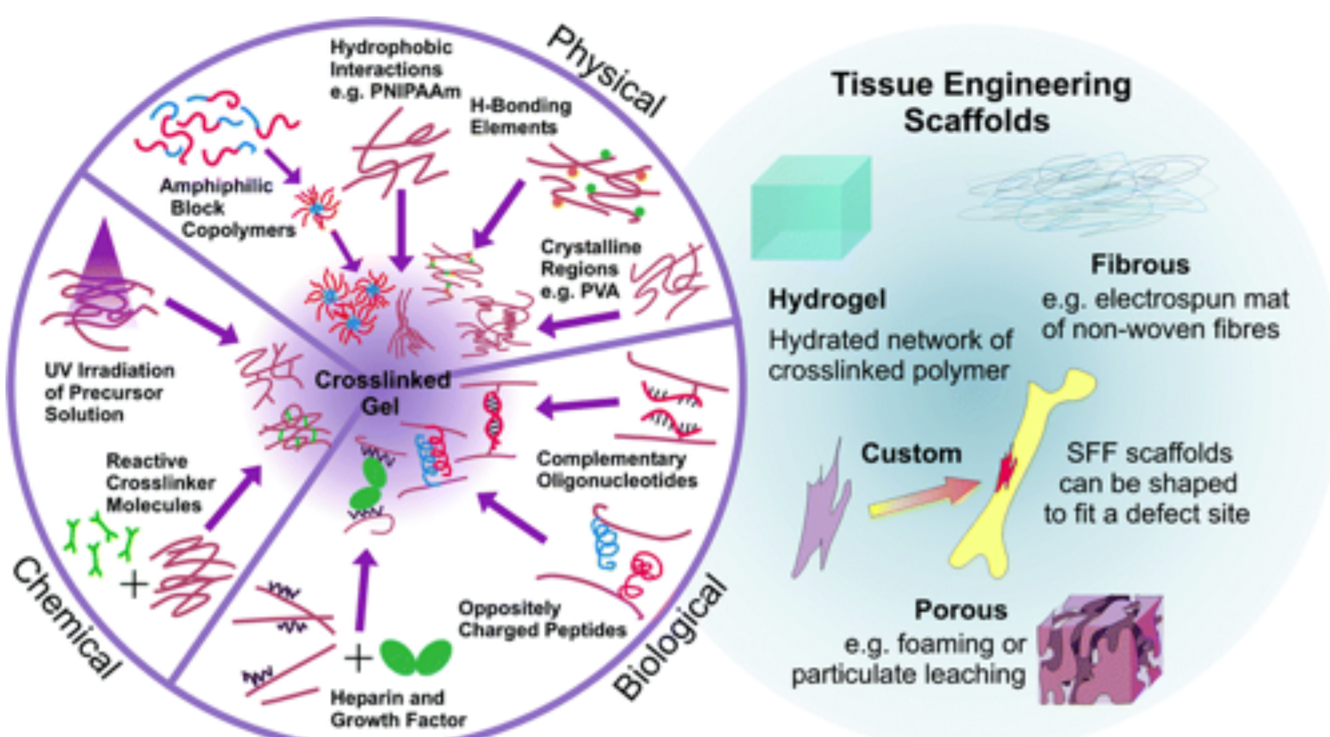
Polymers in biomedical applications

polymers as drug carriers to cancer cells: targeted delivery- reduced side effects



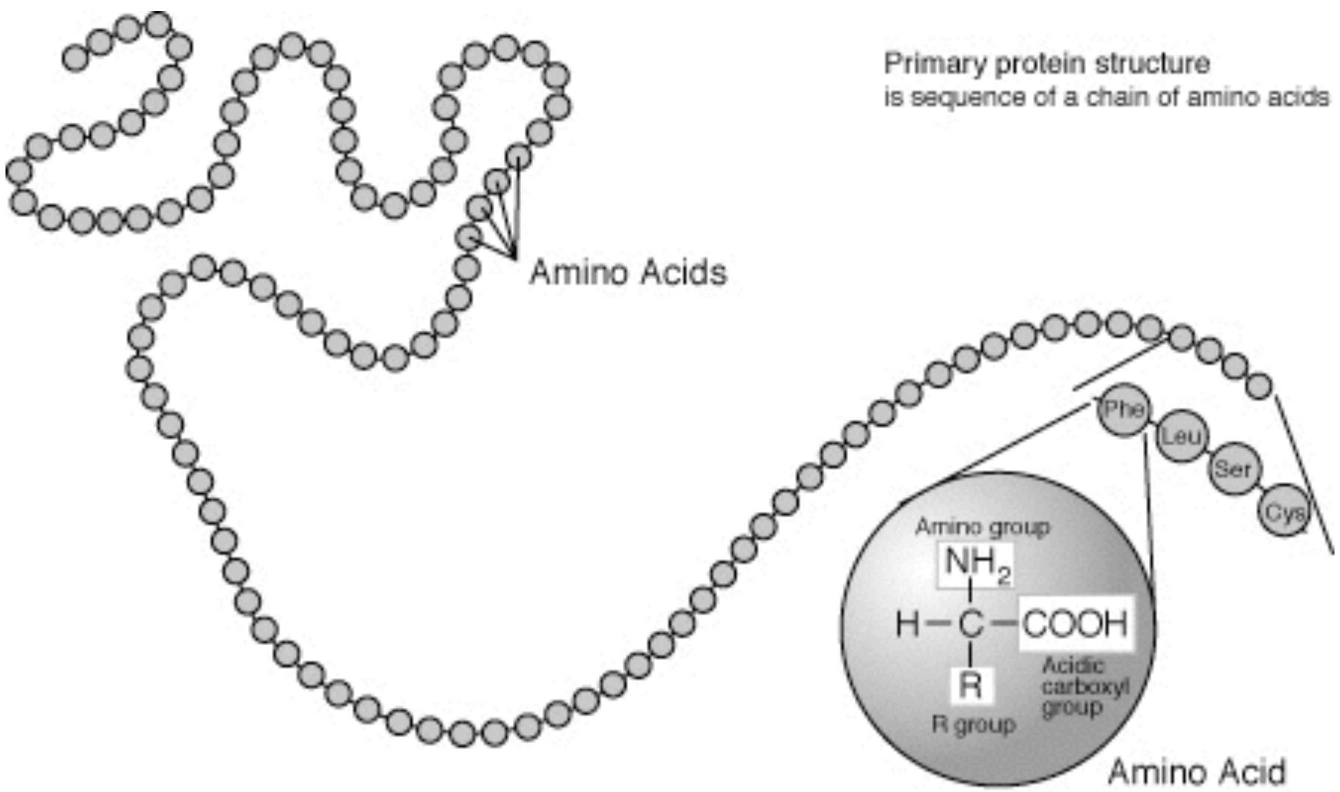
N. Kamaly, et al *Chem. Soc. Rev.*, 2012, **41**, 2971.

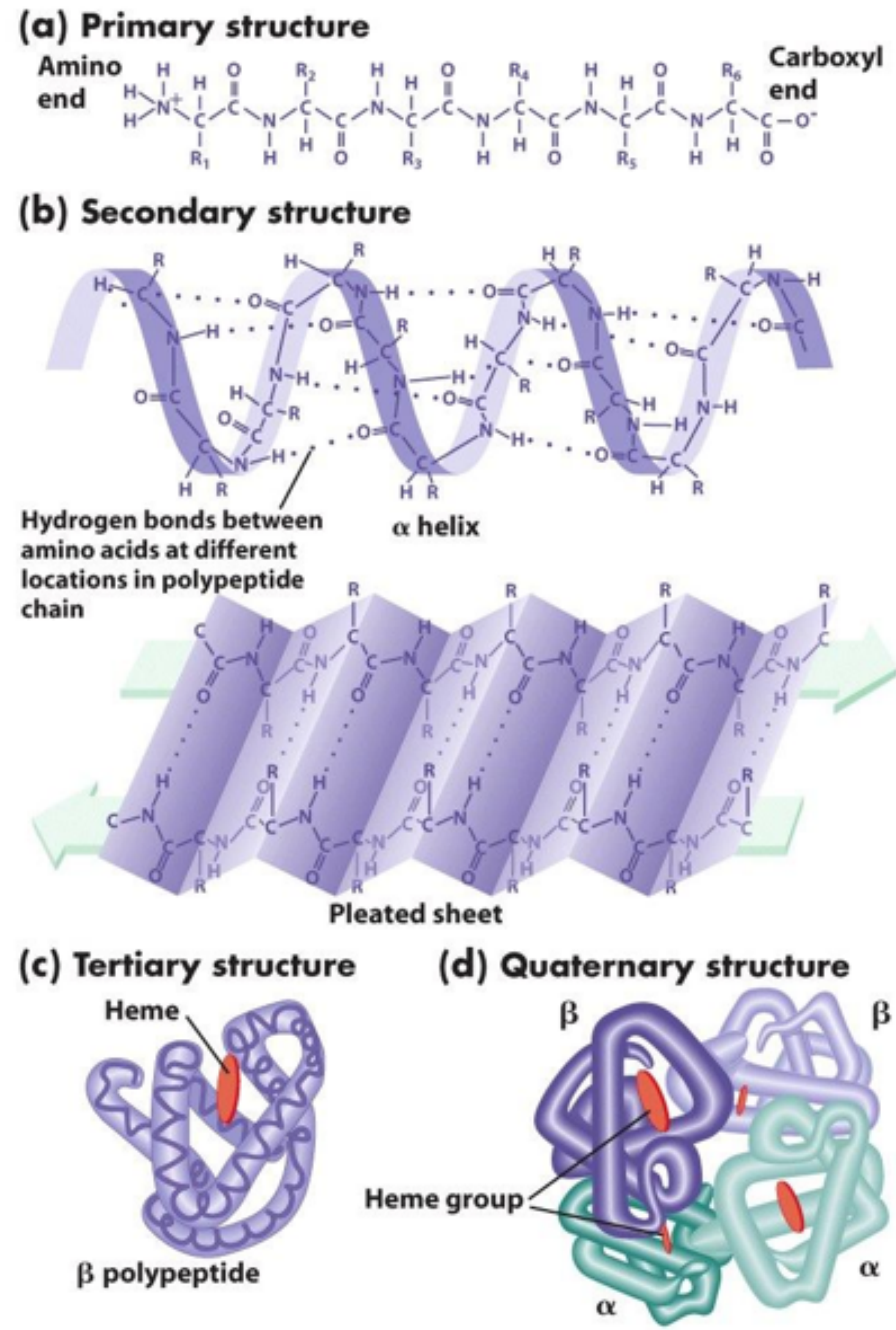
polymers for tissue engineering: regeneration of tissue, implants etc.



What is a polymer? Biopolymers

Proteins are also polymers

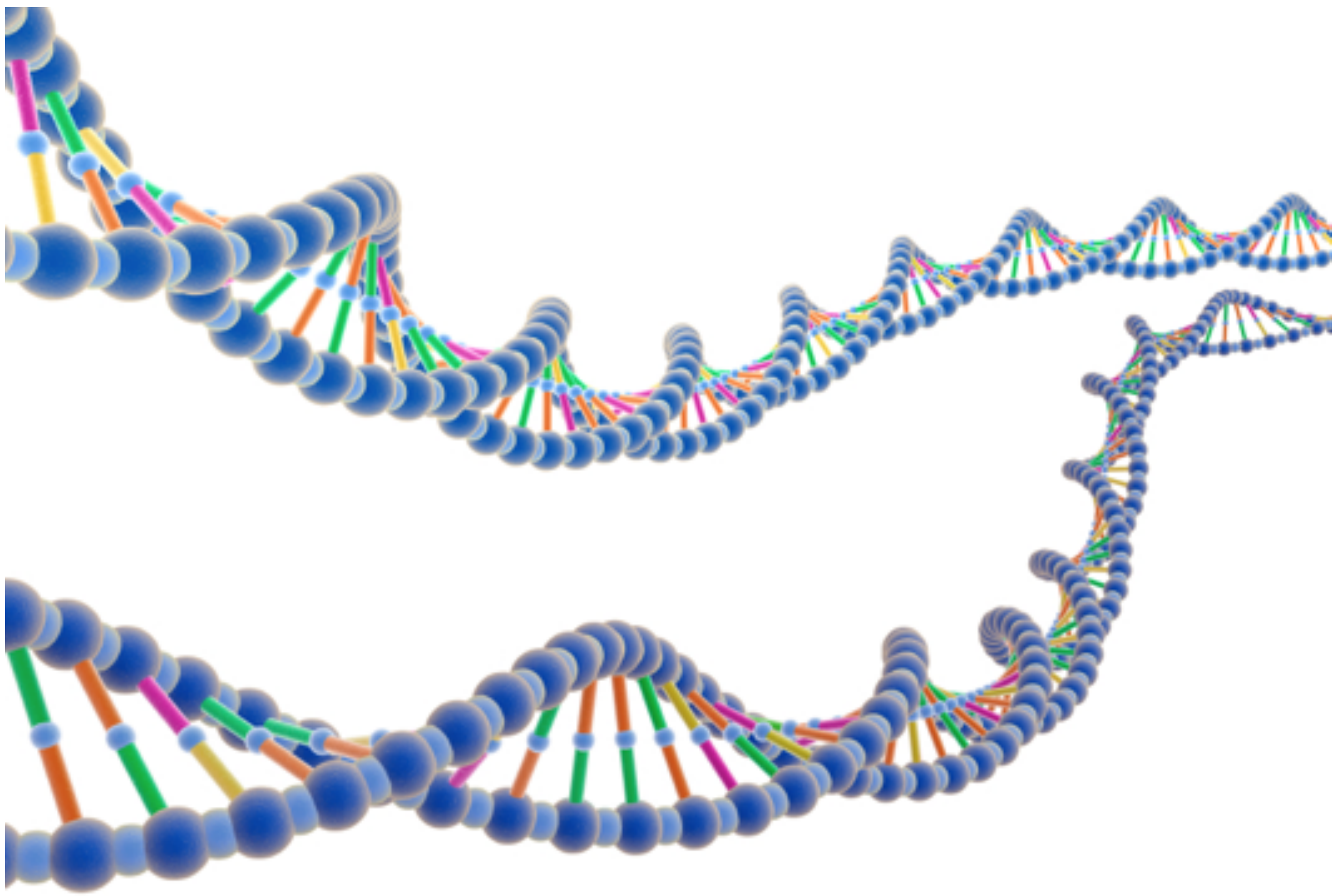


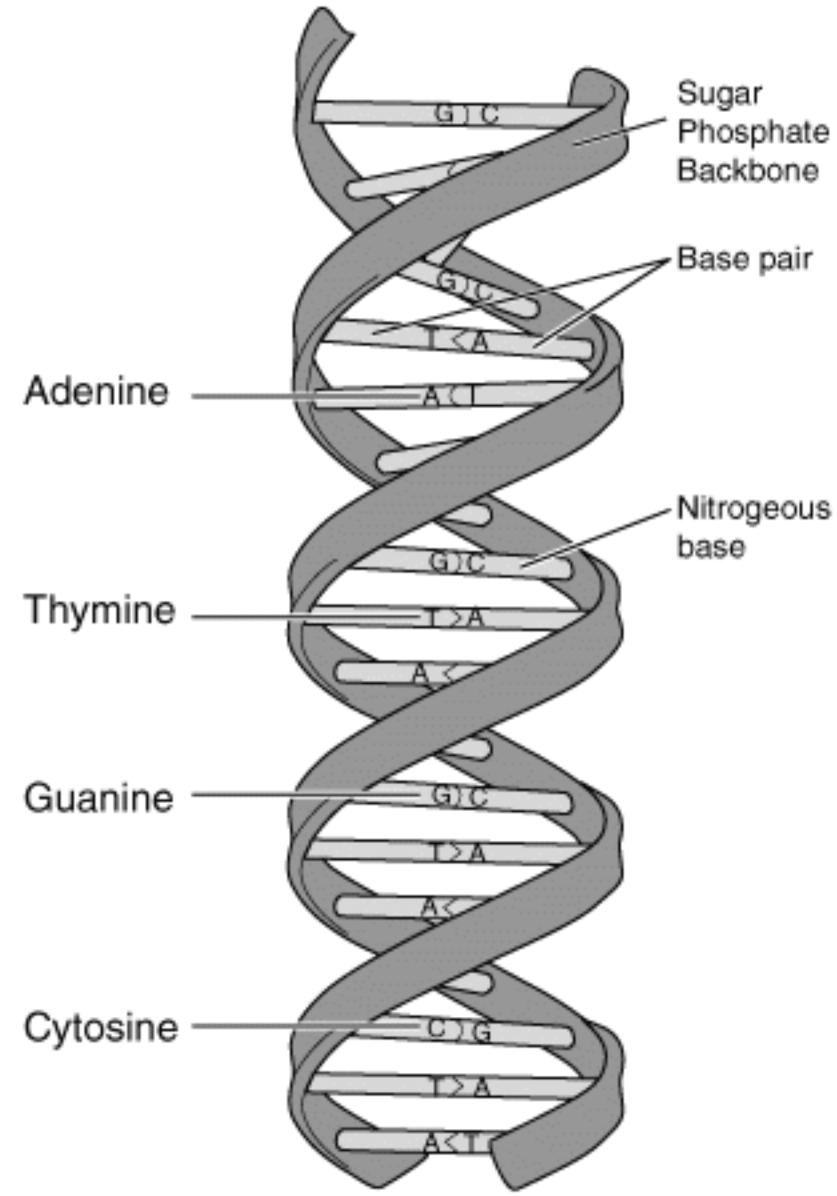


Proteins are polymers with distinct sequences of amino acids- encodes the structures

What is a polymer? Biopolymers

DNA is also a polymer





Distinct sequences of four bases - dictate functions and action in the body- encodes life

Modern polymer science: nanomaterials for advanced technologies

self-assembly

molecular engineering

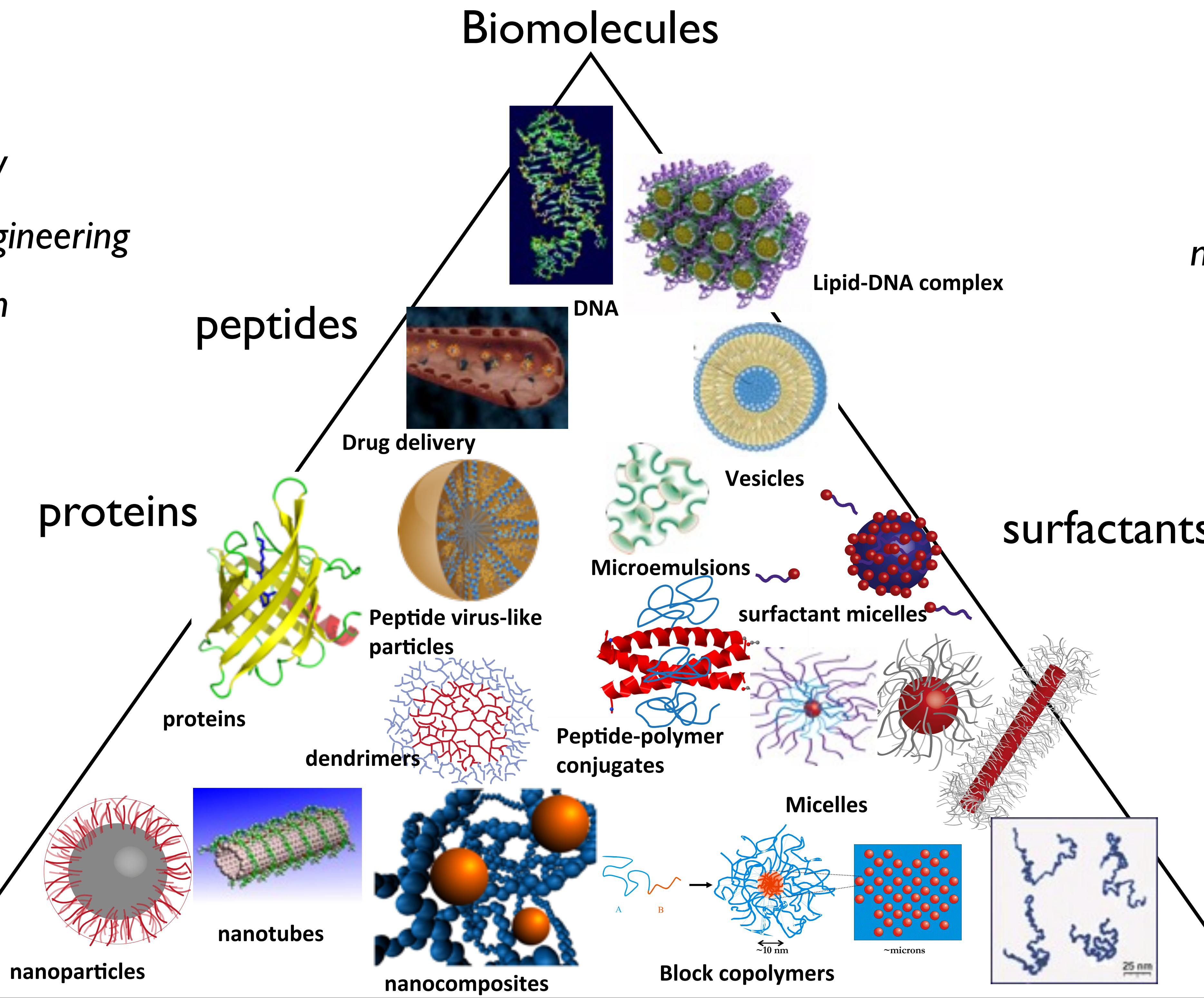
complexation

equilibrium

non-equilibrium

kinetic pathways

dynamics



colloids

polymers

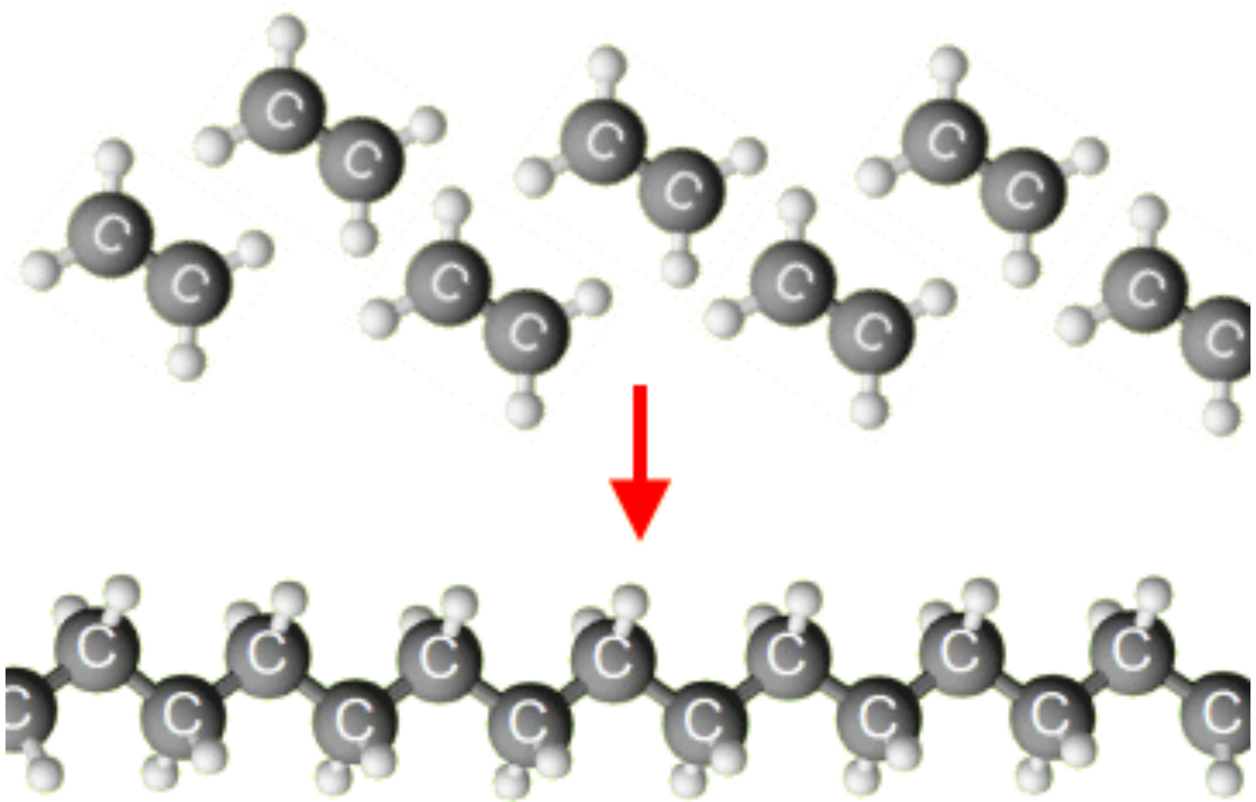
structure, thermodynamics

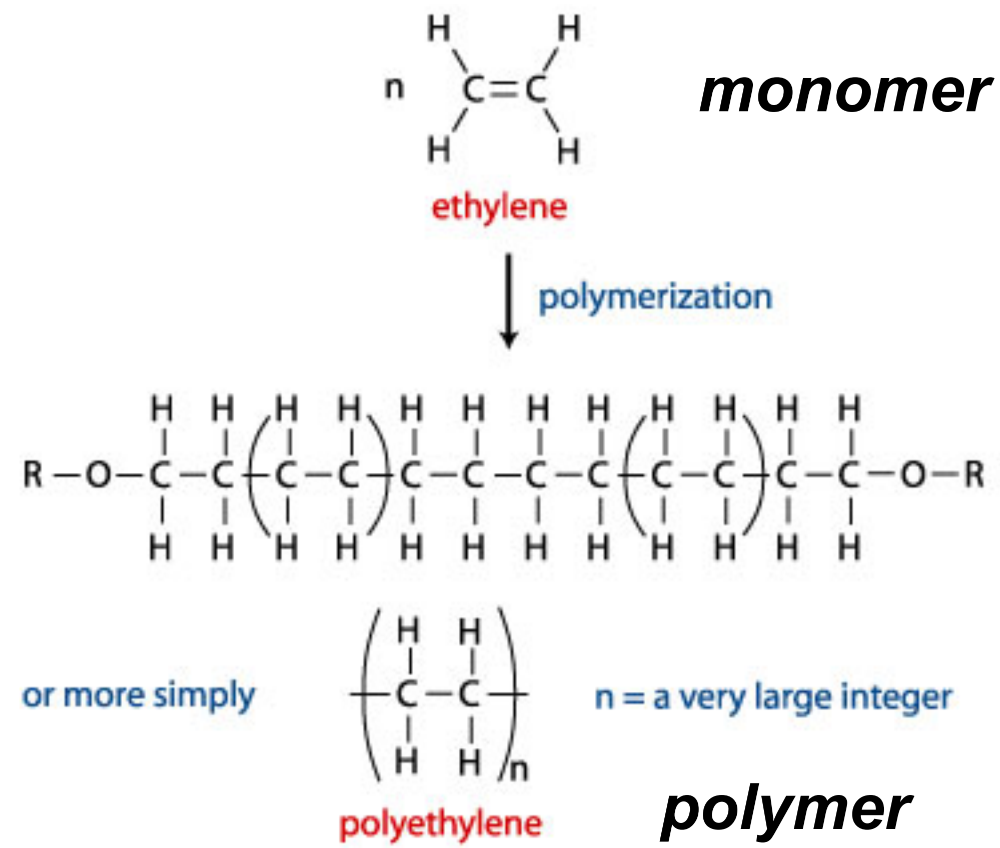
Polymers: Basics

What is a polymer?

Chain-like molecules: synthetic poly(ethylene) as an example

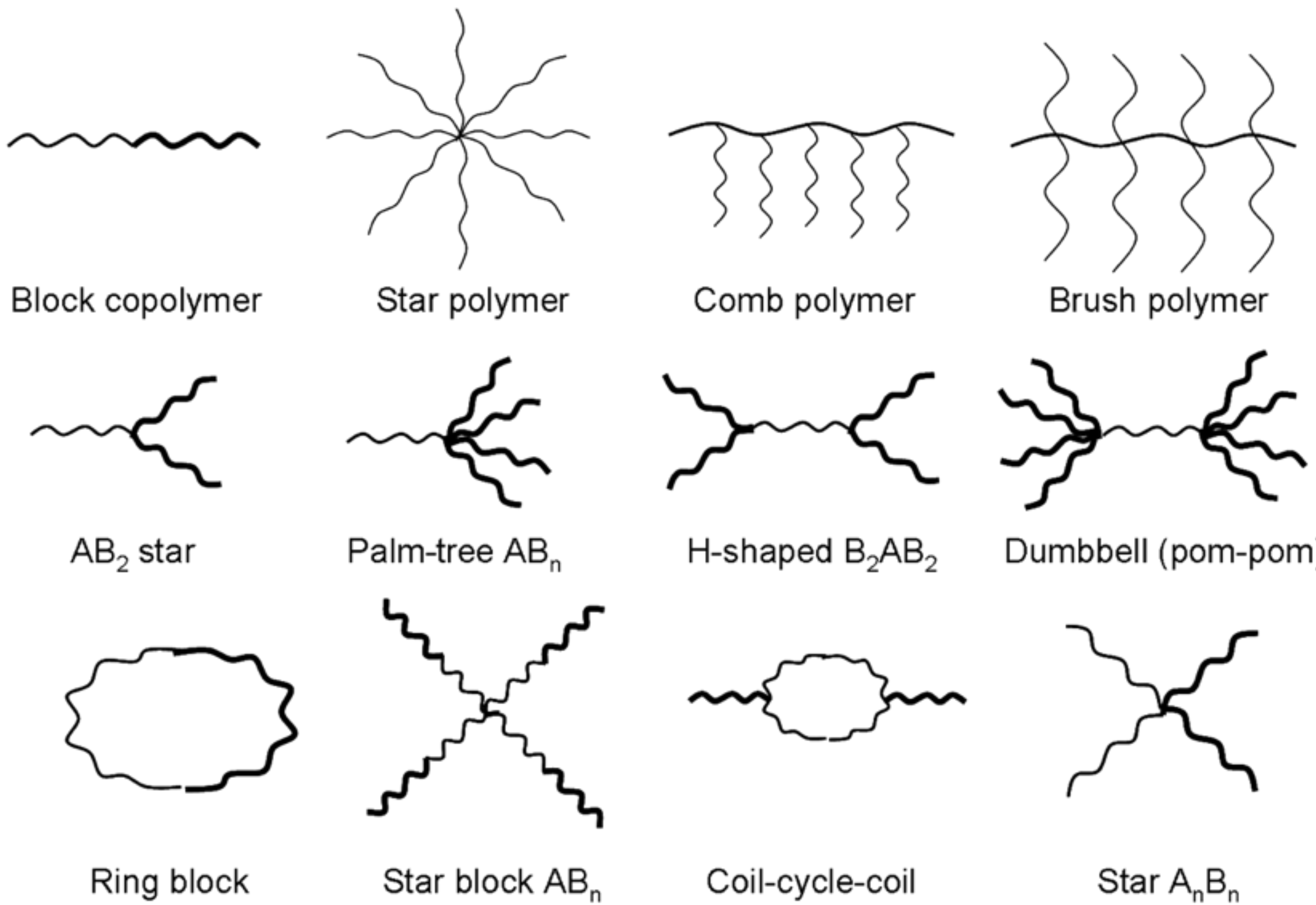
Ethylene to poly(ethylene)





What is a polymer?

chain-like molecules: other topologies/branches



Polymers: when does a molecule become a polymer?

Example: n-alkanes C_nH_{2n+2}

Gas

methane
ethane
propane
butane

Liquid

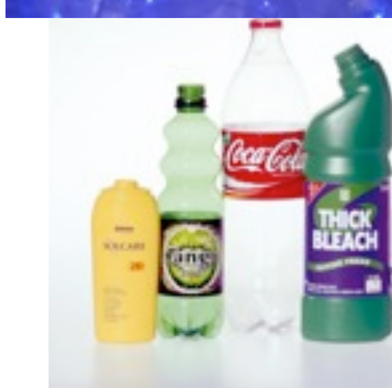
5 to 19
Carbons

Wax

20 to 40
Carbons

Plastic

40 or more
Carbons «poly
(ethylene)»



What is happening when the chain gets longer?

Polymers: n-alkanes C_nH_{2n+2}

Example: n-alkanes

Increased chain-length leads to:

- increased *van der Waals* interactions (electrons/molecule)
- increased melting point/crystallinity
- increased topological interactions (entanglement, knots..)
- decreased molecular mobility

⇒ **change in viscosity and material properties**

Polymers: five characteristic properties

1. **connectivity and chain entanglement**- *enhanced mechanical strength*

2. **reduced configurational (mixing) entropy** - *different polymers tend to demix*

3. **Importance of conformational entropy** - *chain deformation leads to rubber-like restoring force*

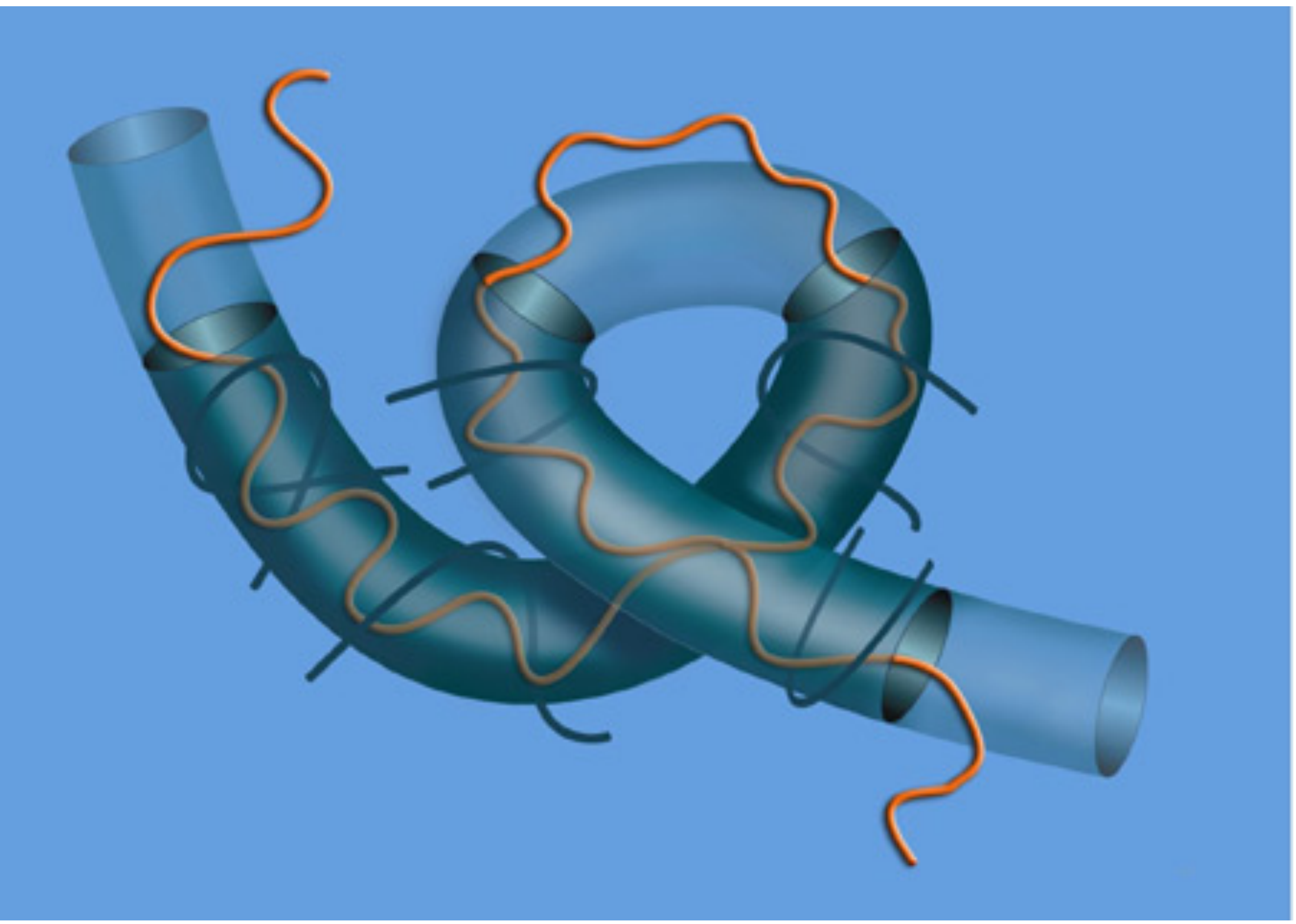
4. **enhanced intermolecular forces per molecule**- *high cohesion energies*

5. **low mobility (slow dynamics)** - *high viscosity and elasticity*

Polymers: chain connectivity and entanglements

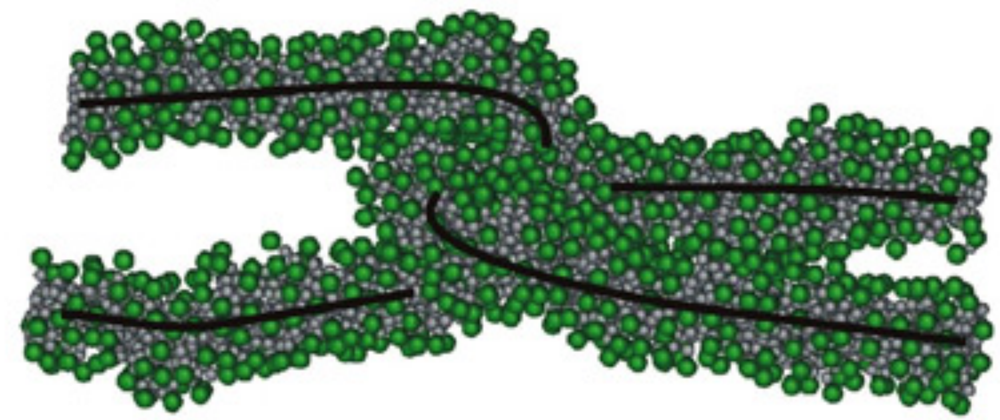
Connectivity and entanglement:

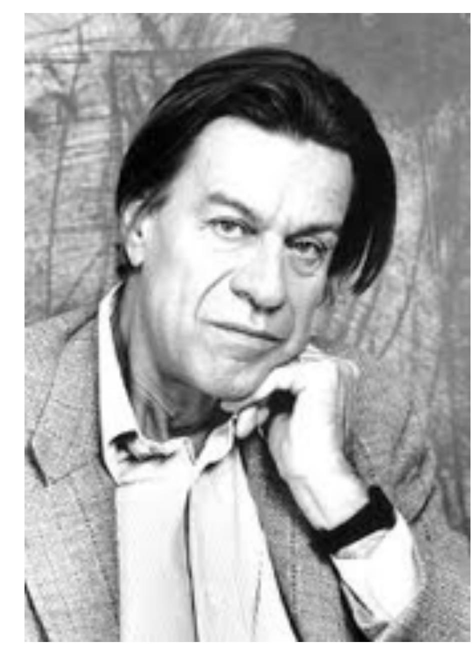
Entanglement - «tube model»



Other polymer chains entrap/limit a single chain- effectively a «tube»

Physical cross-links:
«molecular knots»

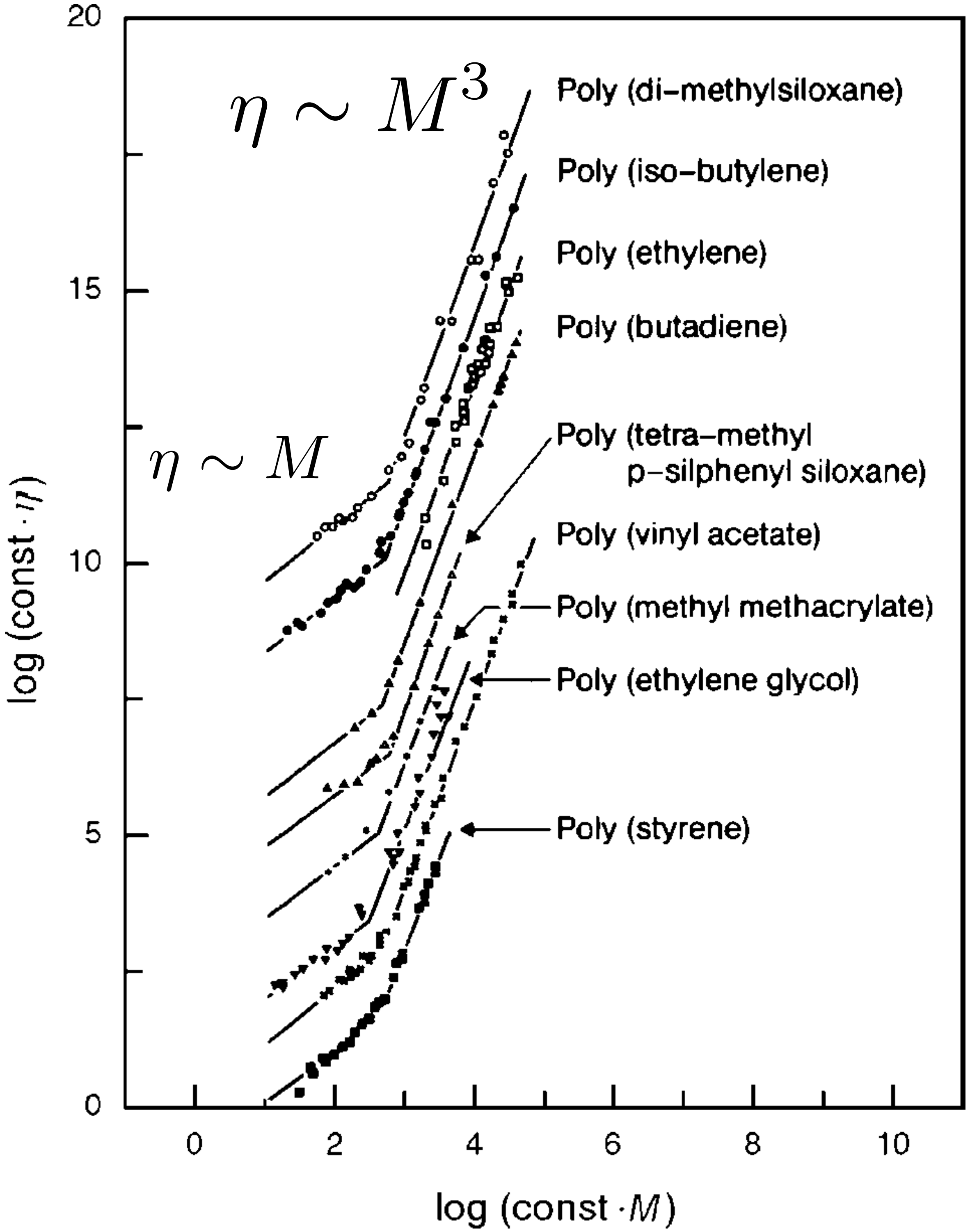




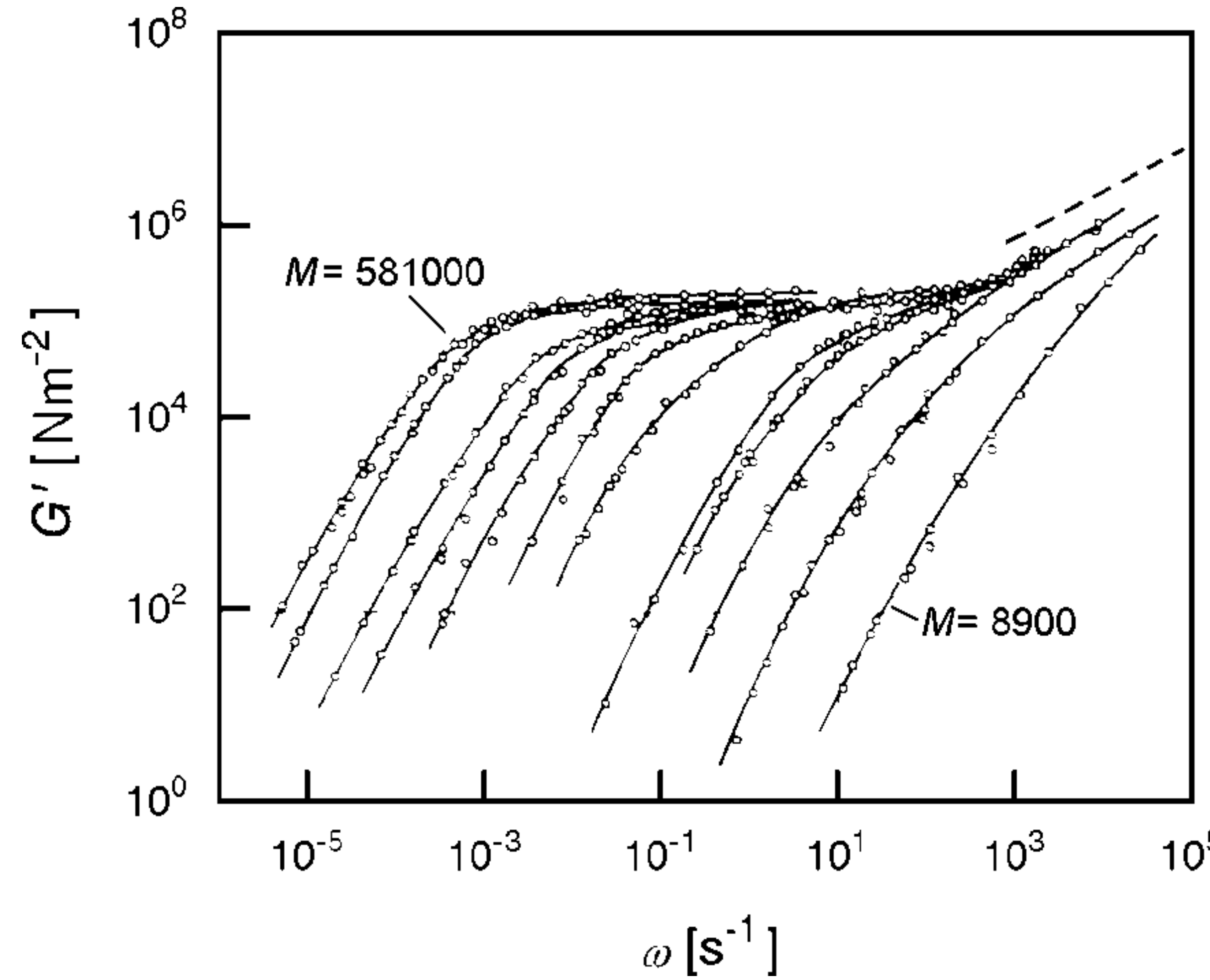
Pierre-Gilles de Gennes
Nobel Prize 1991

Polymers: rheological properties of linear chains

Viscosity



Elastic shear modulus



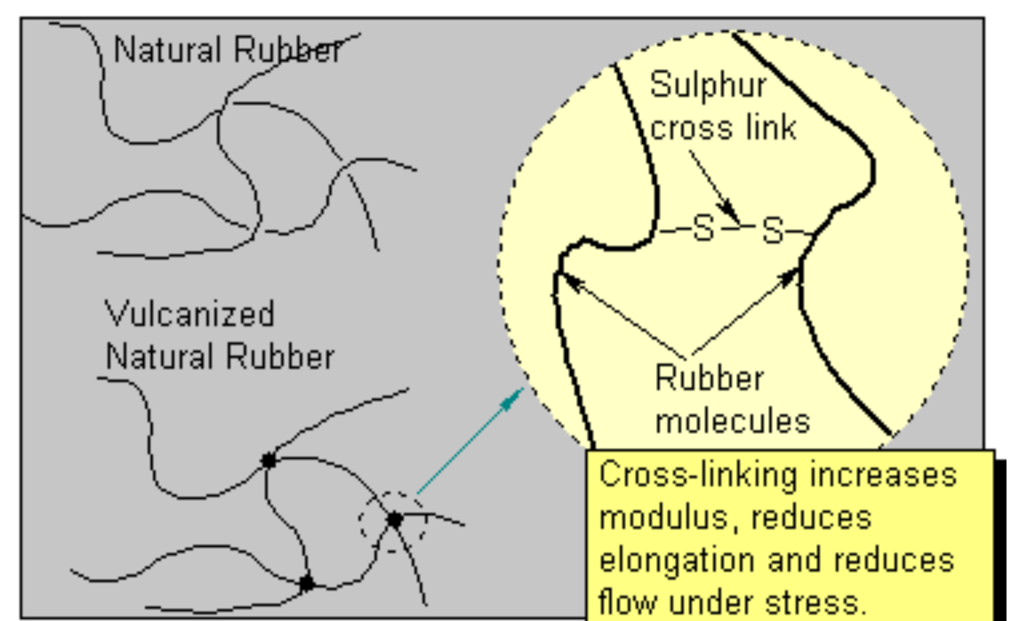
Molecular weight leads to drastic increase in viscosity and elasticity: *even non-covalent bonds leads to network properties!*

Polymers: chemical cross-links

Connectivity: chemical cross-links

1. Polymerization with radicals / multifunctional monomers (branched and cross-linked polymers)

2. Post-polymerization treatment
- i.e. oxidation of sulphur- «vulcanization»

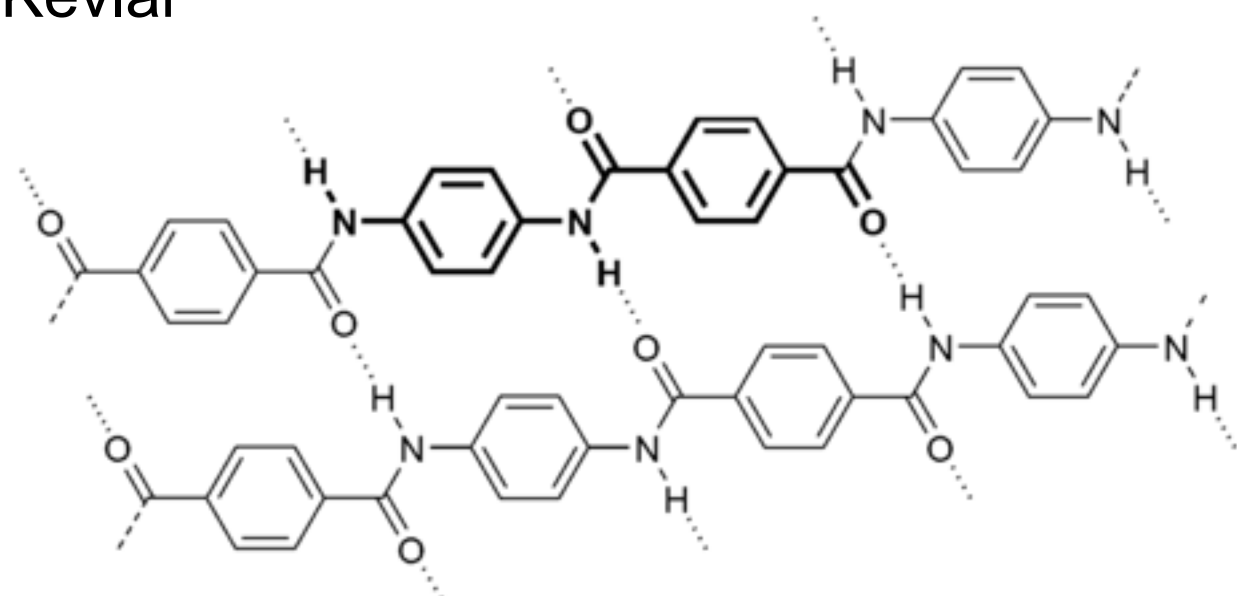


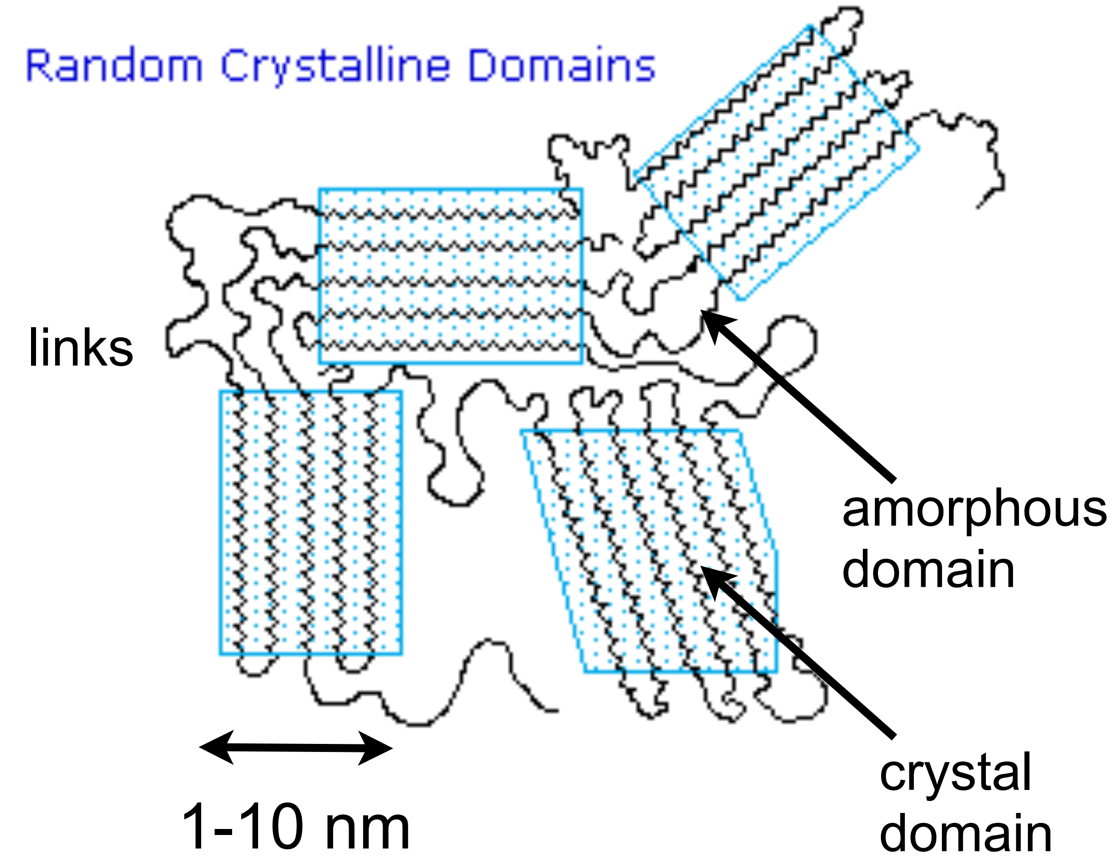
MATTER, The University of Liverpool

Crystallinity in polymers

Nanocrystallinity:

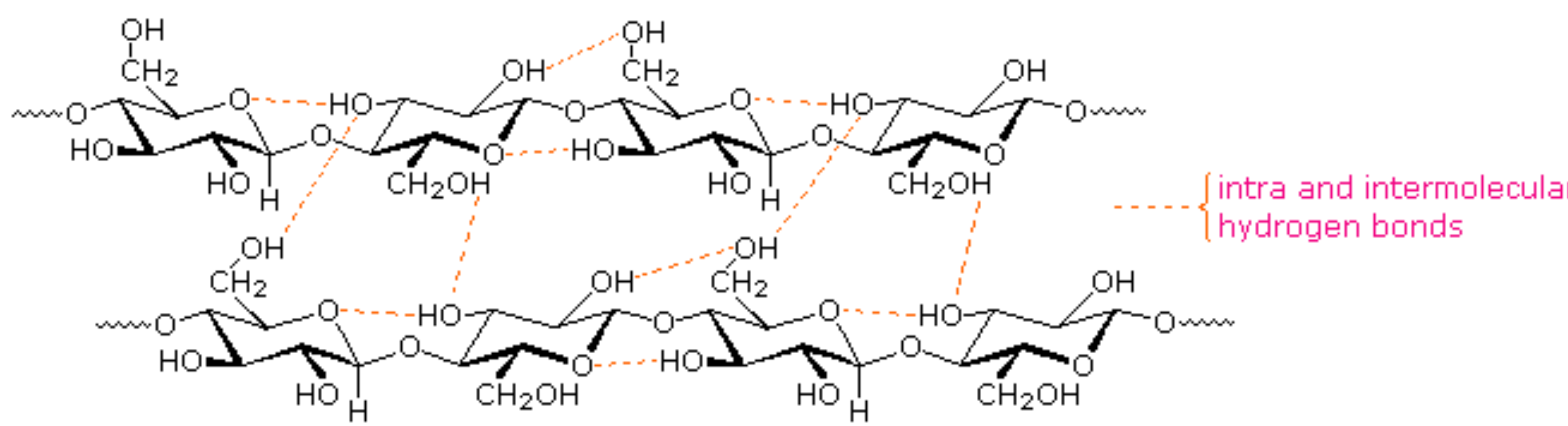
Kevlar





one-component nanostructured system

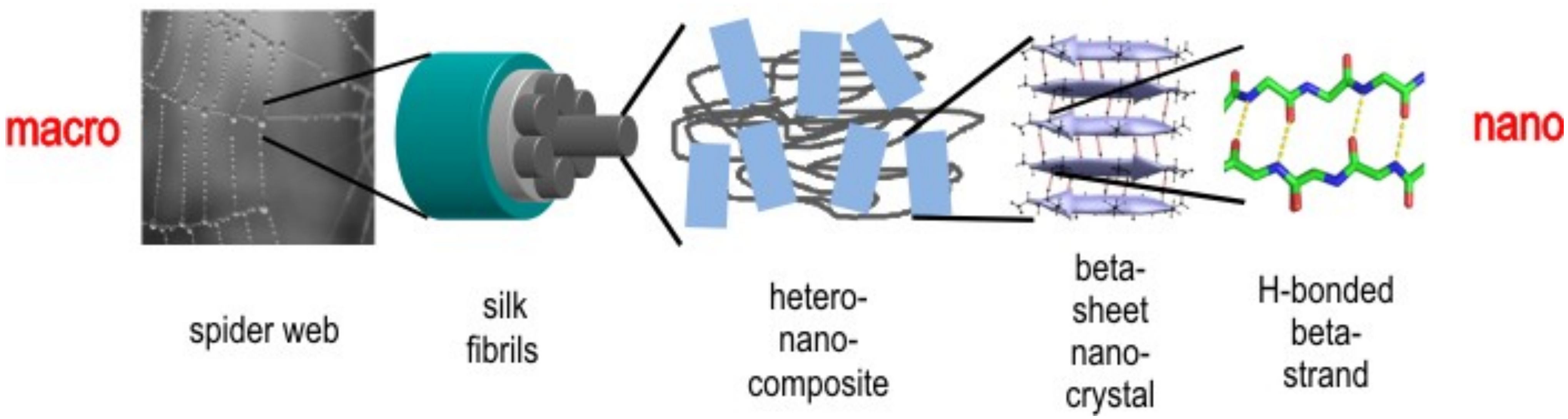
Cellulose
a linear polyglucose
joined by β-1-4 bonds



Crystallinity in polymers

Nanocrystallinity:

Natural composites: «spider web»



Polymers: effect of cross-links on tensile strength

Temperature behaviour

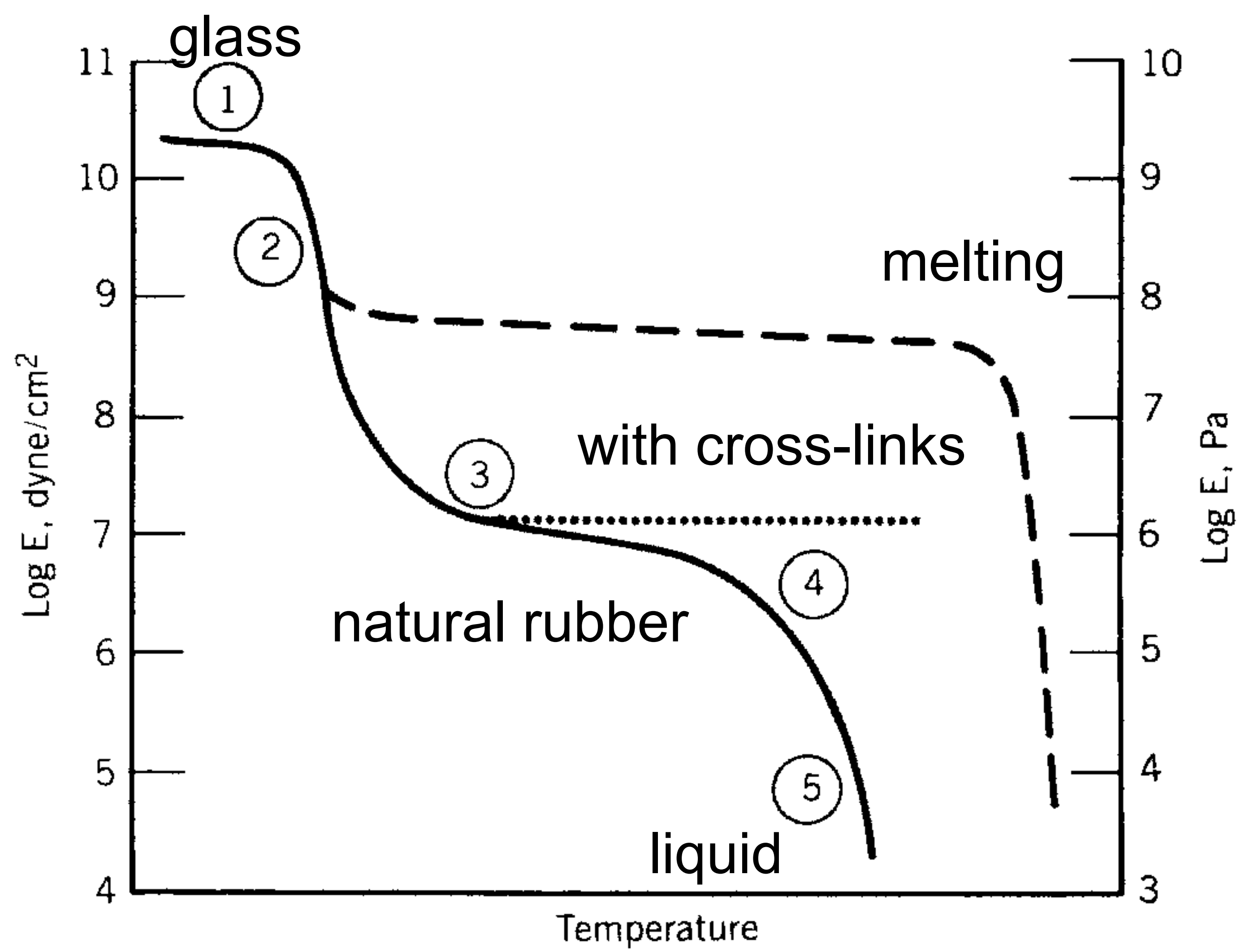


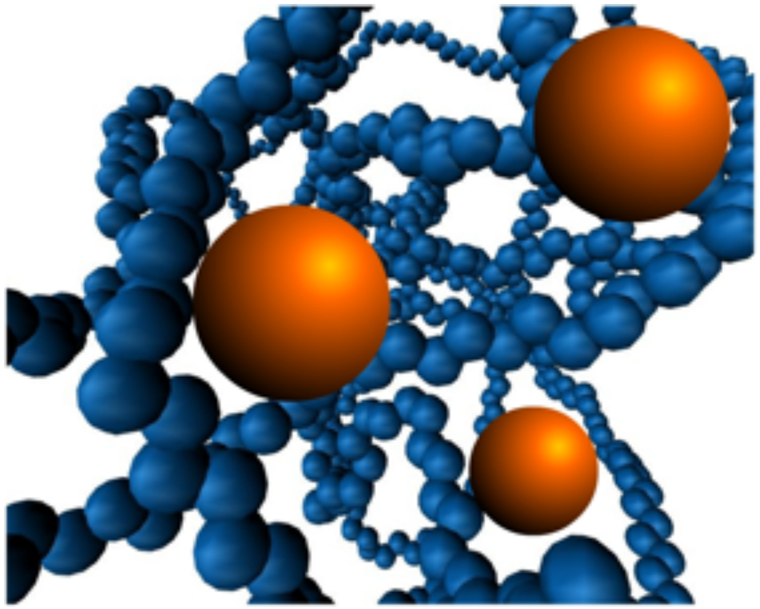
Figure 8.2 Five regions of viscoelastic behavior for a linear, amorphous polymer. Also ill trated are effects of crystallinity (dashed line) and cross-linking (dotted line).

Gert Strobl

The Physics of Polymers

Polymers: nanostructrures

Nanocomposites: polymers and nanoparticles



= polymer + nanoparticles (inorganic/organic)

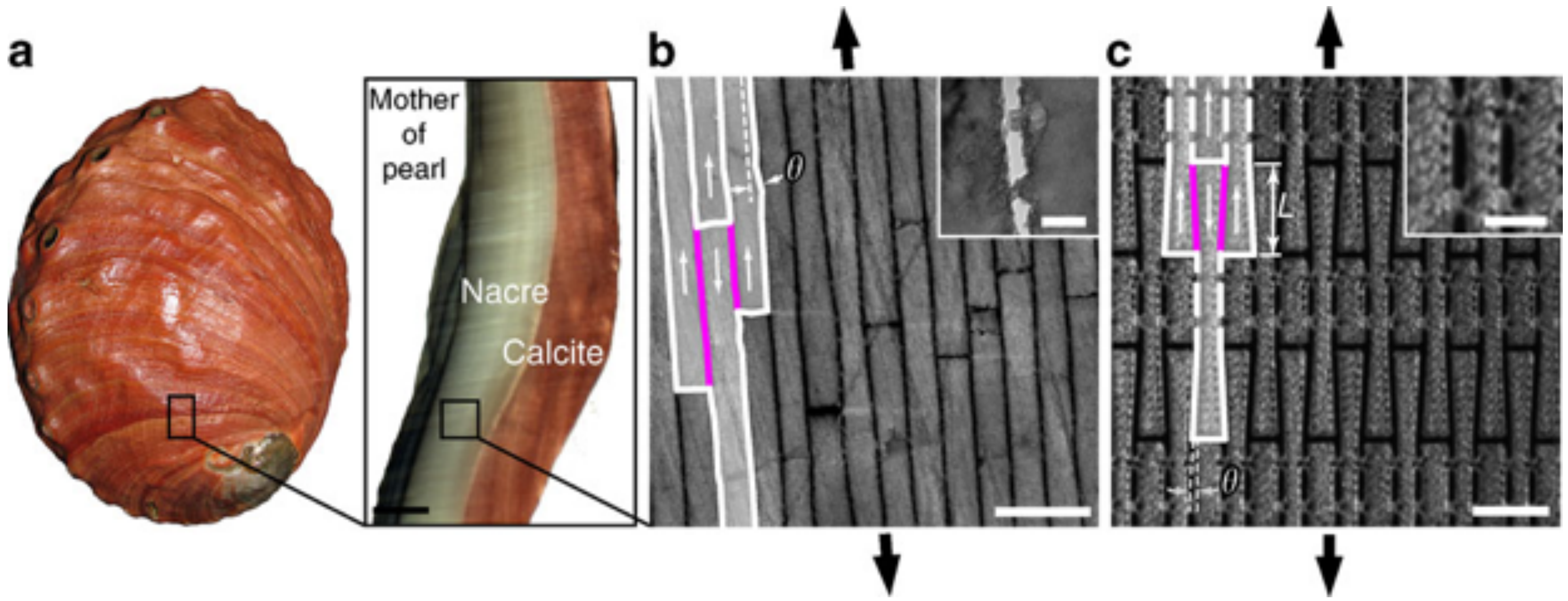
1. Light weight materials with high strength

2. High resistance to fracture - polymers absorb and dissipate energy

3. Functional materials with engineered properties : for e.g. photovoltaics

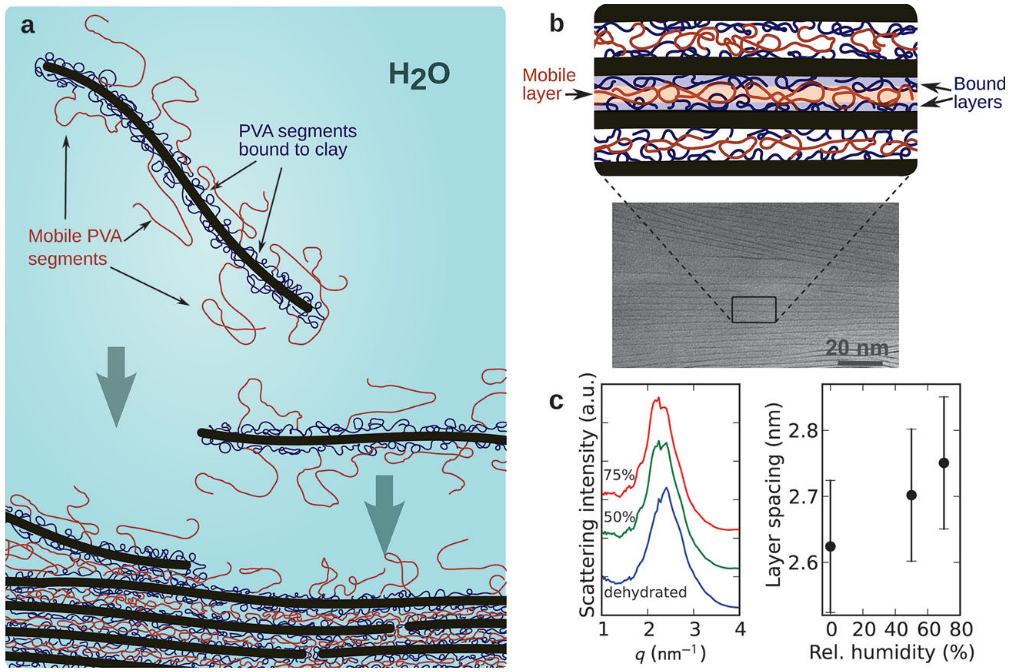
Nanocomposites: polymers and nanoparticles

Natural composites: «nacre»- $CaCO_3$ platelets with biopolymers



H. D. Espinosa, A. L. Juster, F. J. Latourte, O. Y. Loh, D. Gregoire, and P. D. Zavattieri, *Nature Communications*, 2011, **2**, 173–9.

Artificial nacre composites: clay with poly(vinyl alcohol)



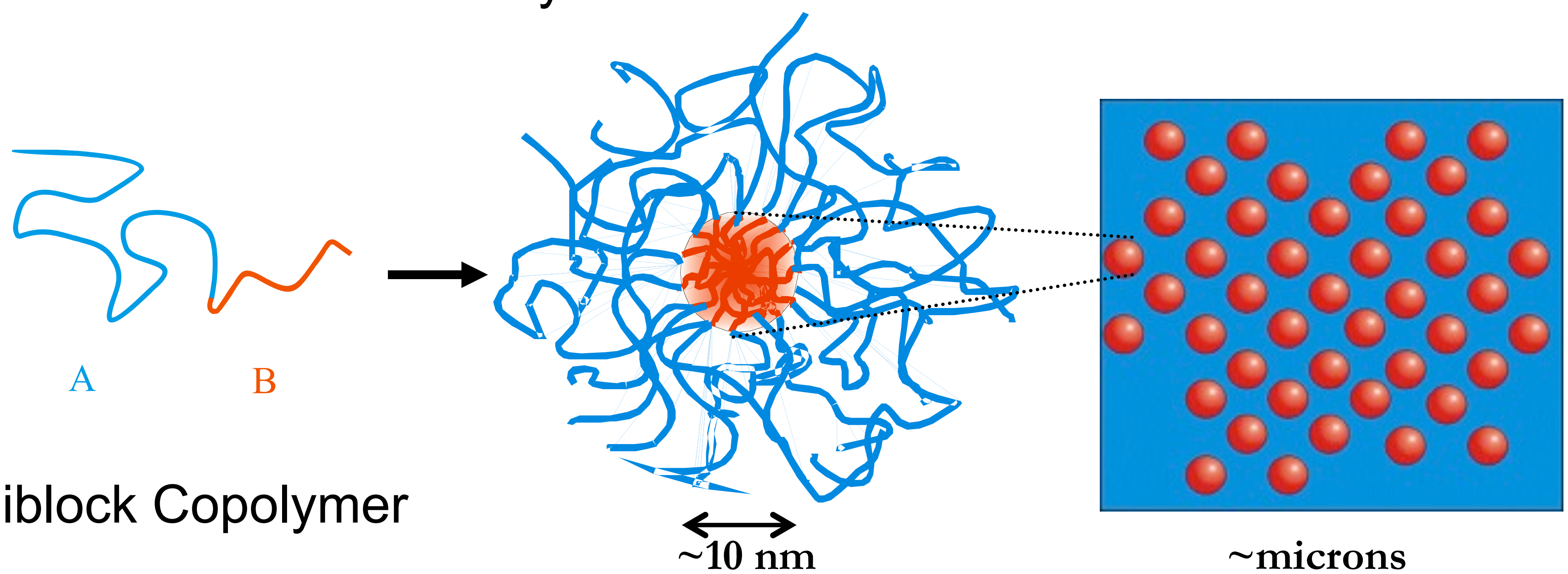
Wide range of parameters control the properties

- dispersibility and distribution
- interactions between particle/polymers
- nanostructure and crystallinity
- humidity
- >Etc..

T. Verho, M. Karesoja, P. Das, L. Martikainen, R. Lund, A. Alegría, A. Walther, and O. Ikkala, *Adv. Mater.*, 2013, **25**, 5055–5059.

Nanostructured polymers: self-assembly

Hierarchical self-assembly



Enthalpy
(favours demixing)
Driven by incompatibility: enthalpy proportional to number of A/B contacts

-Flory-Huggins (chi-) parameter

$$\chi \equiv (\epsilon_{AB} - \frac{1}{2}(\epsilon_A + \epsilon_B)Z/(k_B T)$$

energy per lattice point

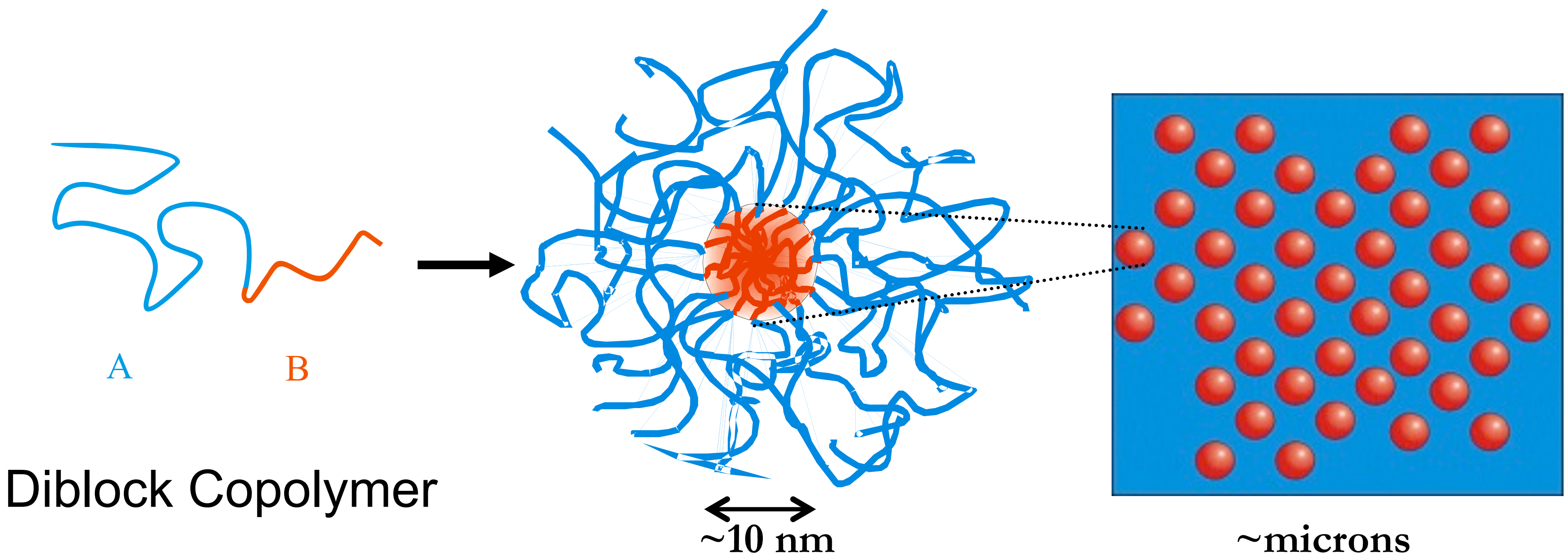
lattice coordination number

$$\Delta H = n_A \Phi_B \cdot k_B T \cdot \chi$$

number of A-segments

Concentration of B-segments

Nanostructured polymers: self-assembly



Entropy of mixing polymers:
(favours random mixing)

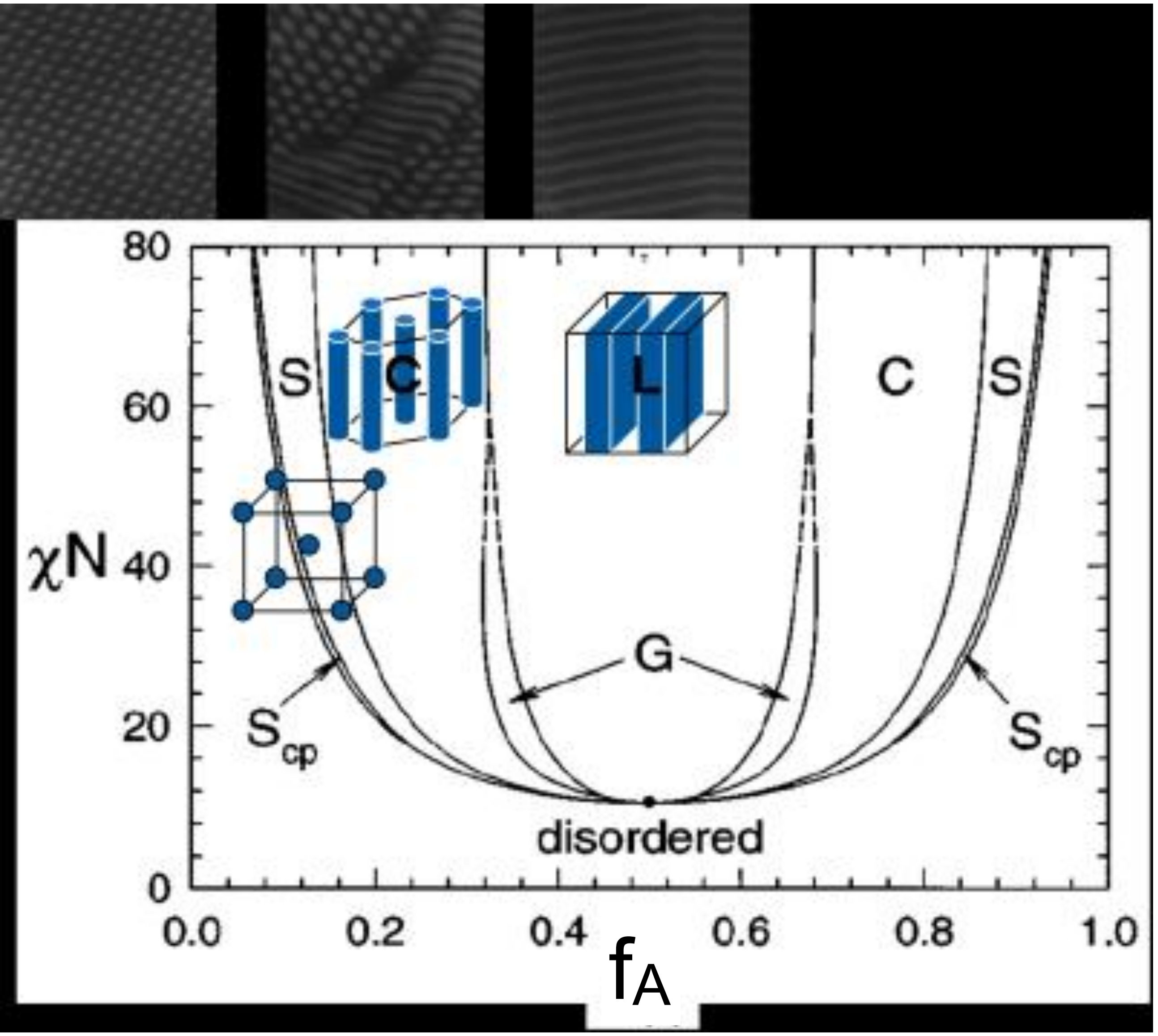
$$\Delta S = k_B \frac{\Phi}{N} \ln \Phi$$

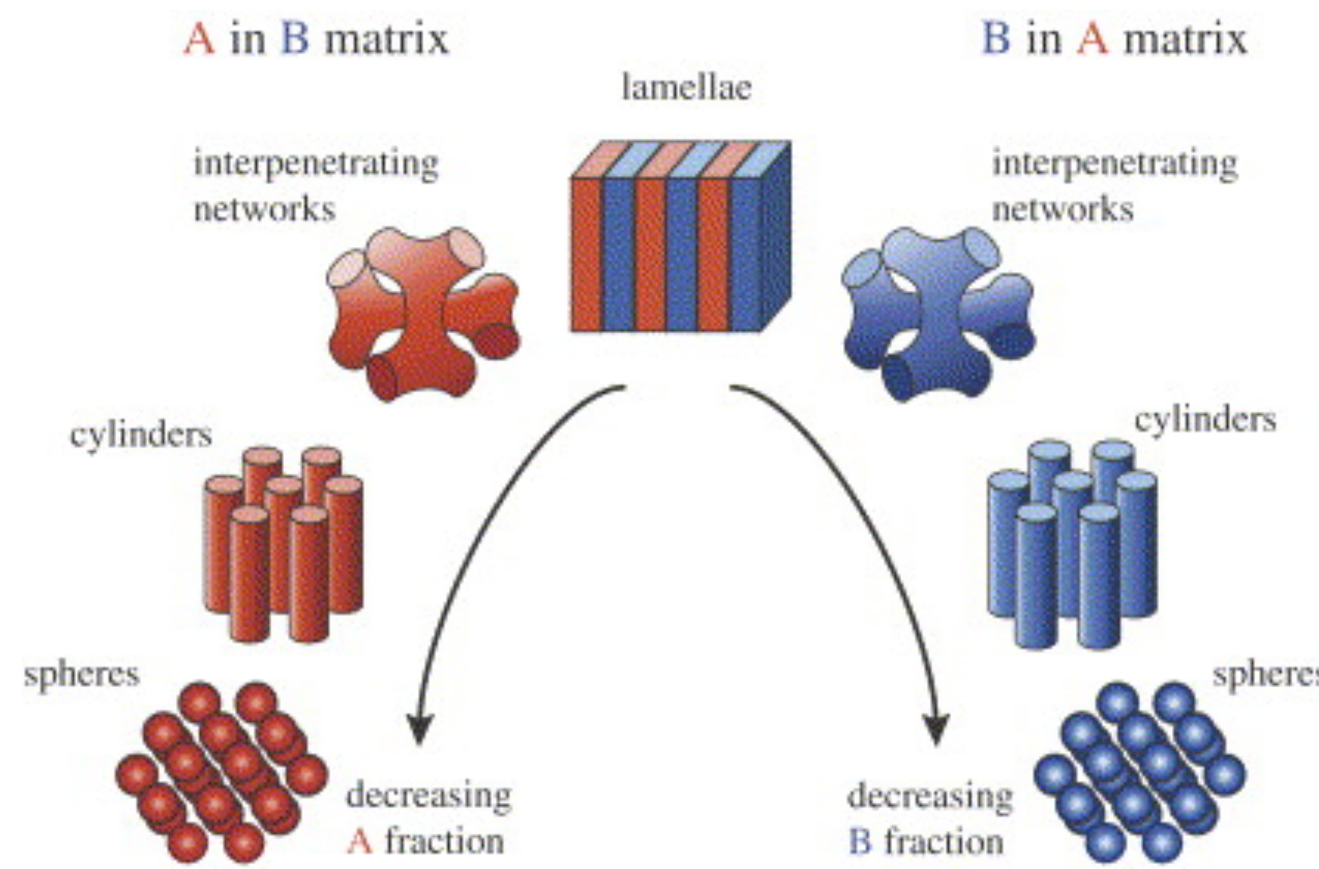
Connectivity
(restricts the phase separation)

nanoseparation governed by:

$$\Delta H / \Delta S \sim \chi N$$

Block copolymer melts: nanostructures



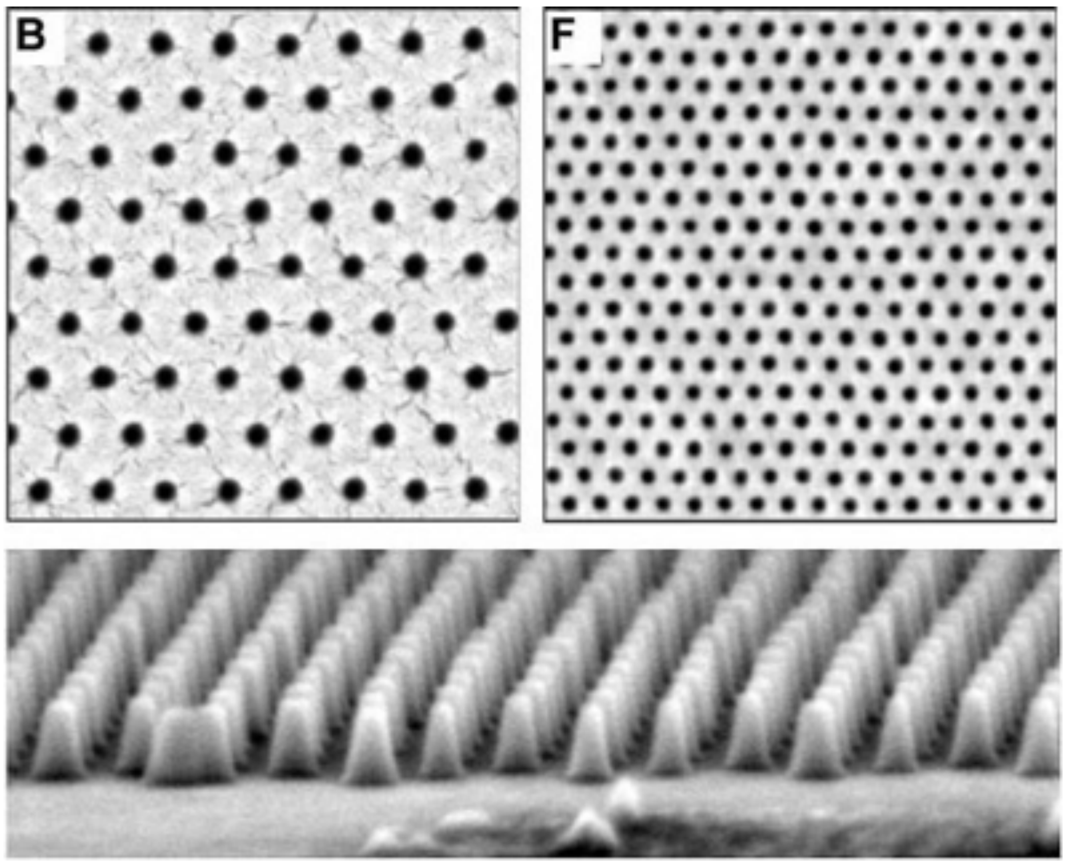


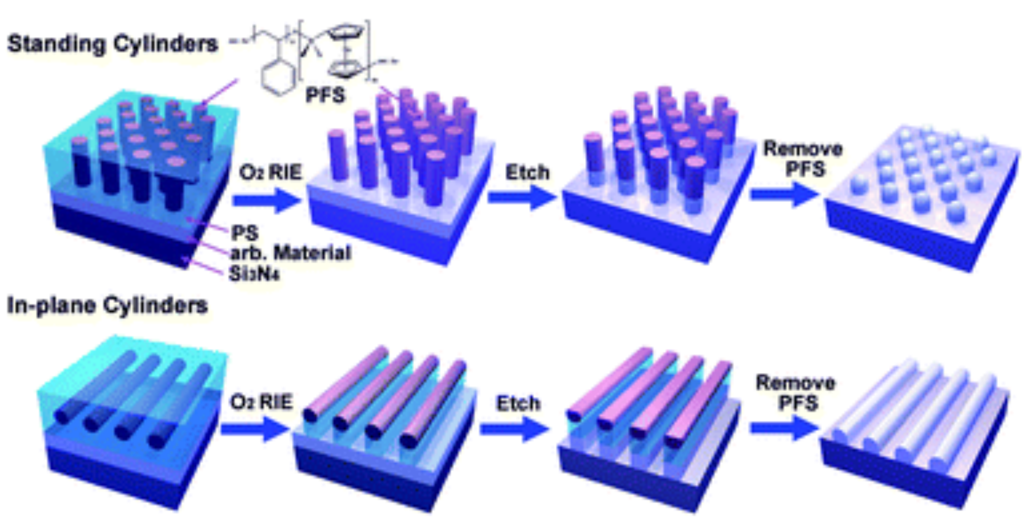
Morphology and size can be accurately tuned via block copolymer composition (f_A), chemistry (χ) and molecular weight (N).

Block copolymer melts: applications

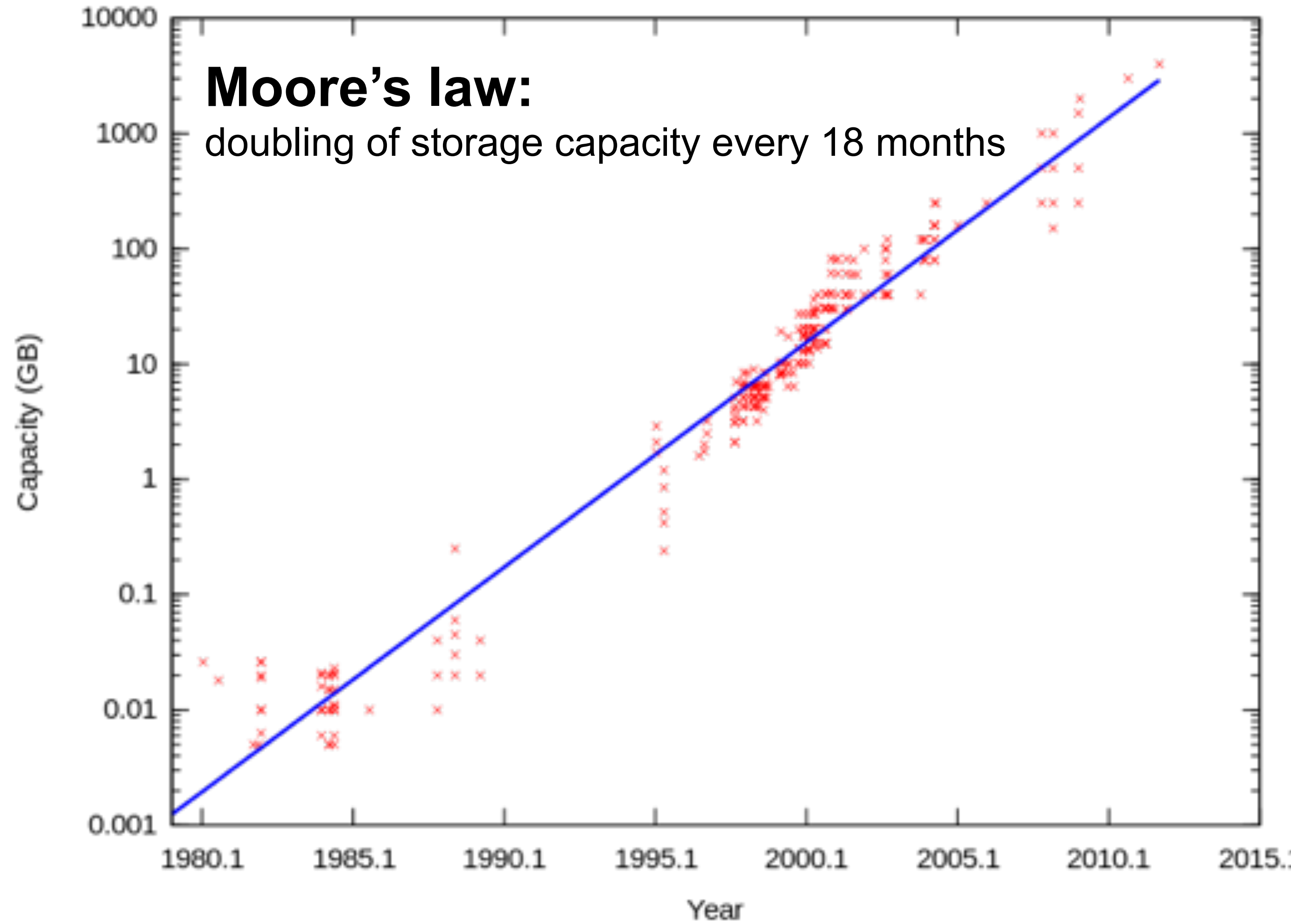
As masks and scaffolds-*nanolitography*

Natural size region:1-10 nm





data storage capacity

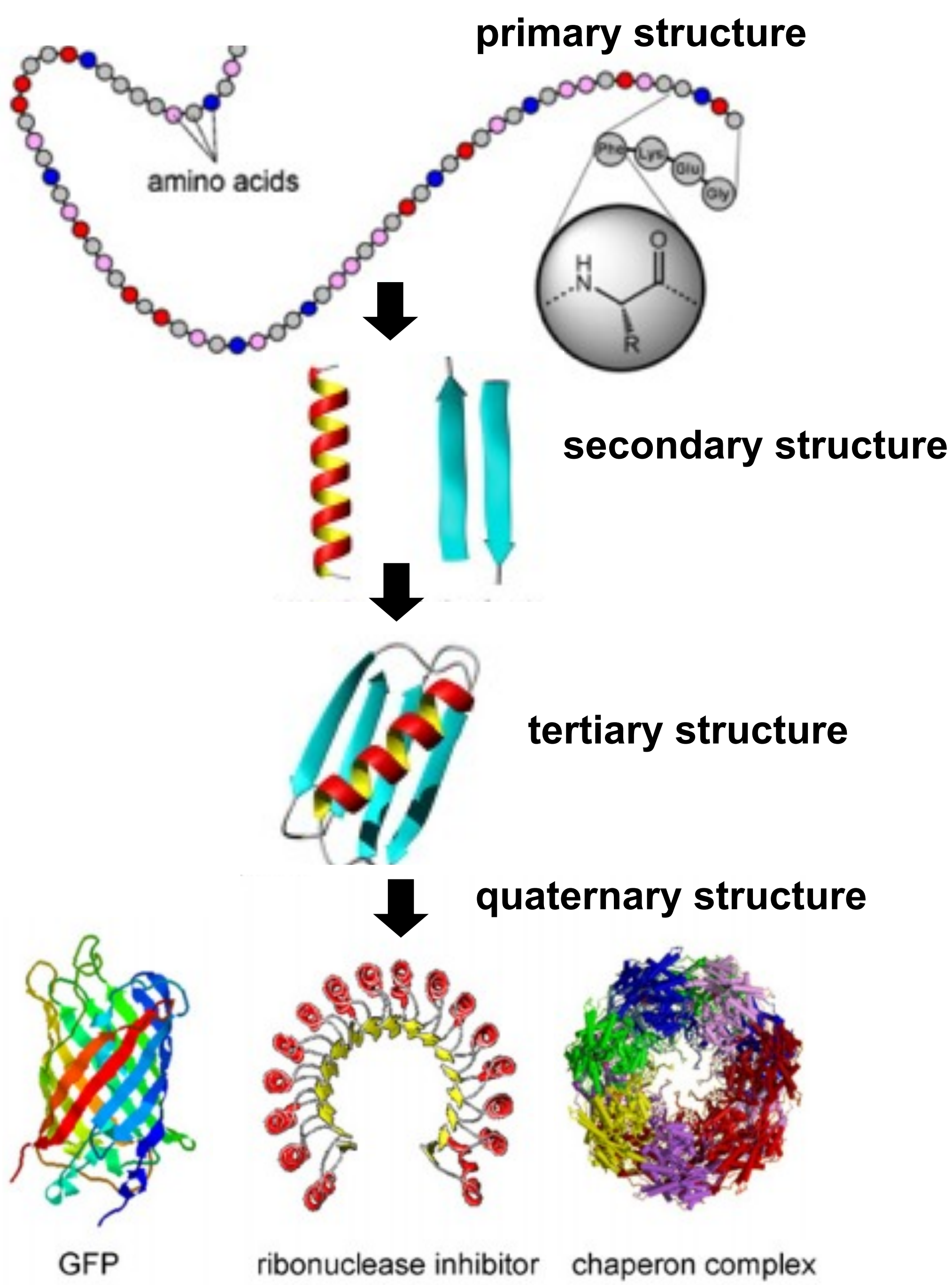


Limit: bits/per area to smaller and smaller areas
Current standard lithographic methods provide absolute limit of 10-20 nm

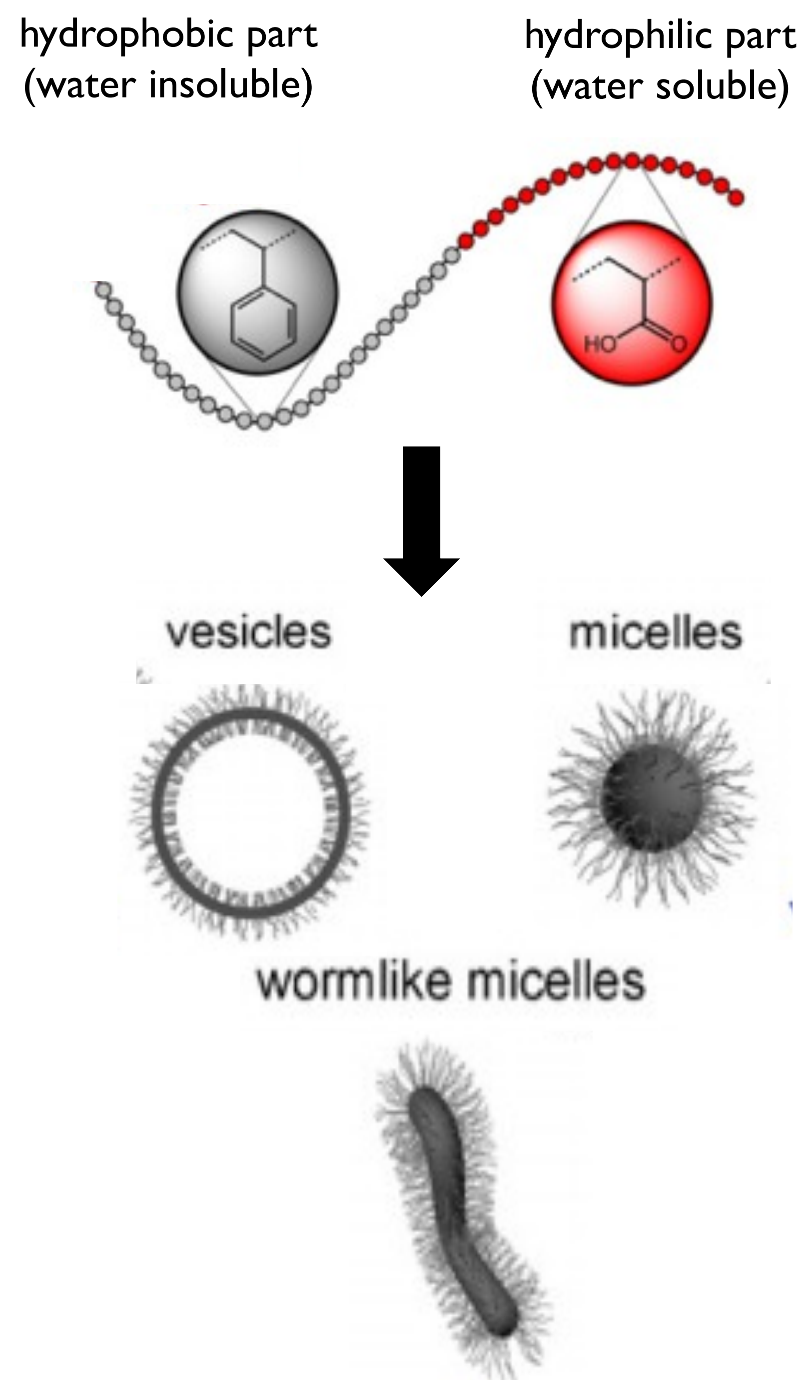
Block copolymers provide higher storage density down to 1 nm!

Polymers: self-assembly

proteins



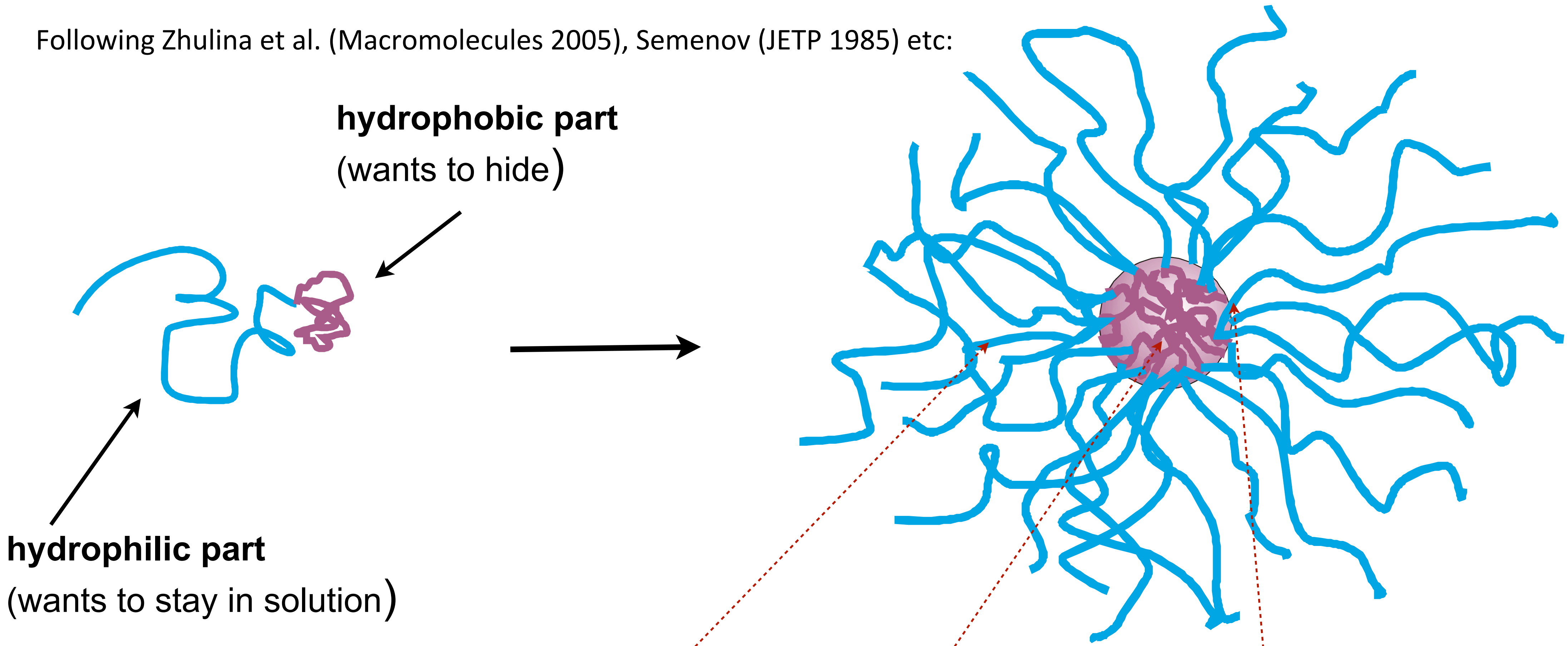
amphiphilic block copolymer



Driven by the unfavourable contact between water and hydrophobic parts of the molecule

Block Copolymer Micelles: *thermodynamics*

Following Zhulina et al. (Macromolecules 2005), Semenov (JETP 1985) etc:

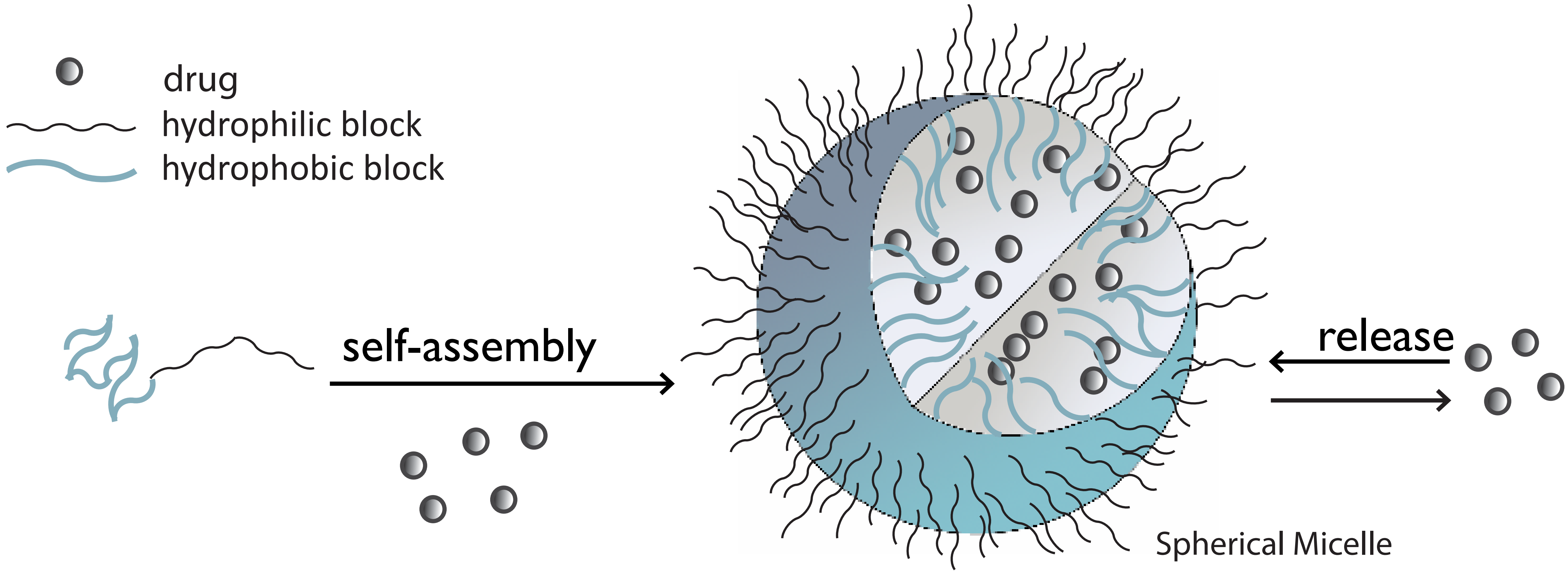


$$F_{\text{micelle}} = F_{\text{corona}} + F_{\text{core}} + F_{\text{int}}$$

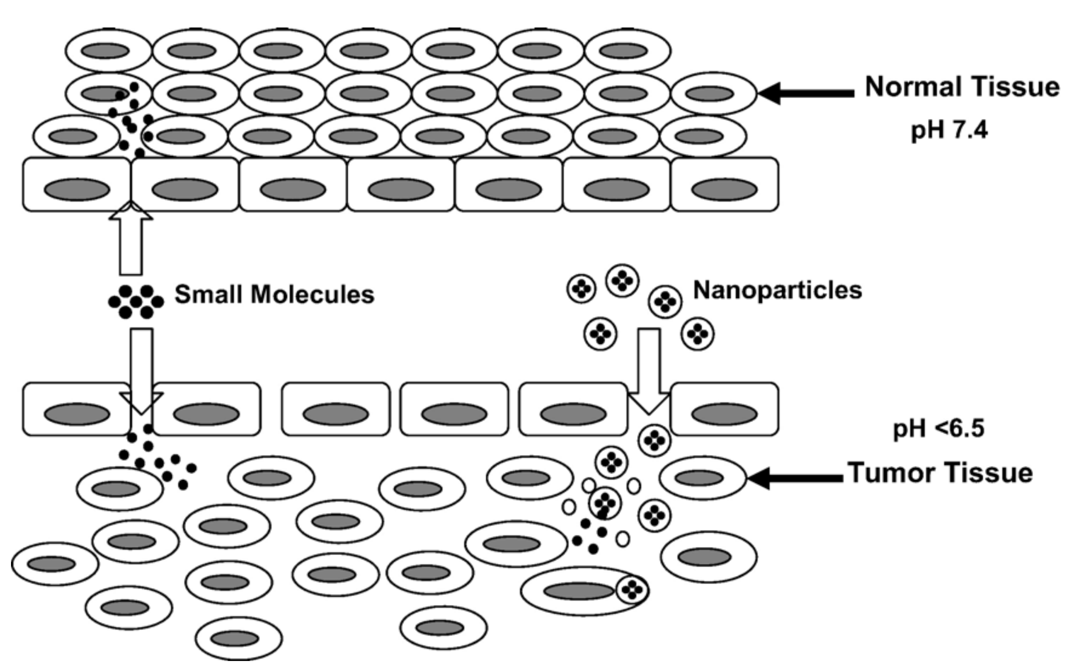
stretching/interaction in corona — stretching of chains in core — surface energy (interfacial tension)

Driven by interfacial tension (F_{int}) - growth is limited by ($F_{\text{corona}}/F_{\text{core}}$)

Polymers as nano-capsules for drug delivery



EPR-effect: enhanced accumulation of nanoparticles in cancer cells

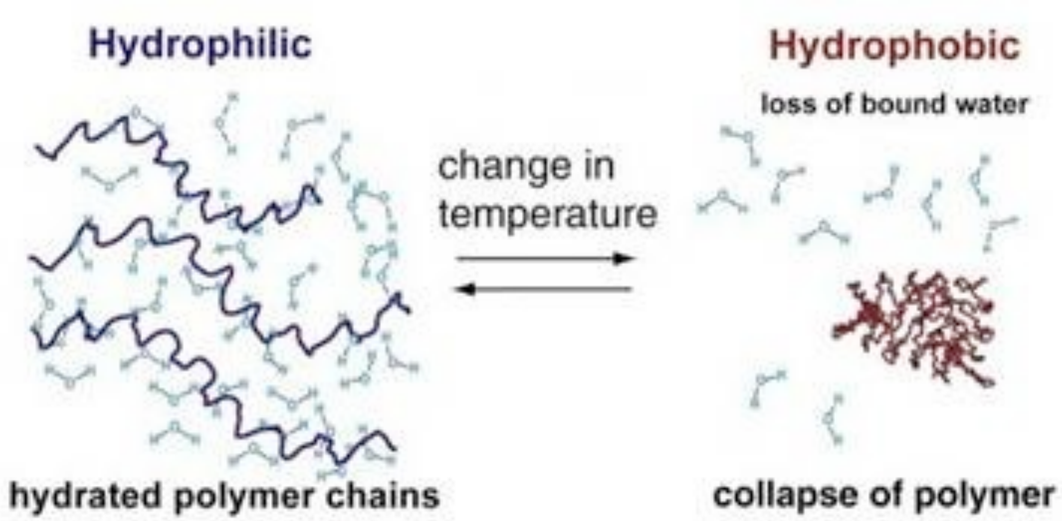


Polymer micelles can deliver therapeutical loads to cancer tissues

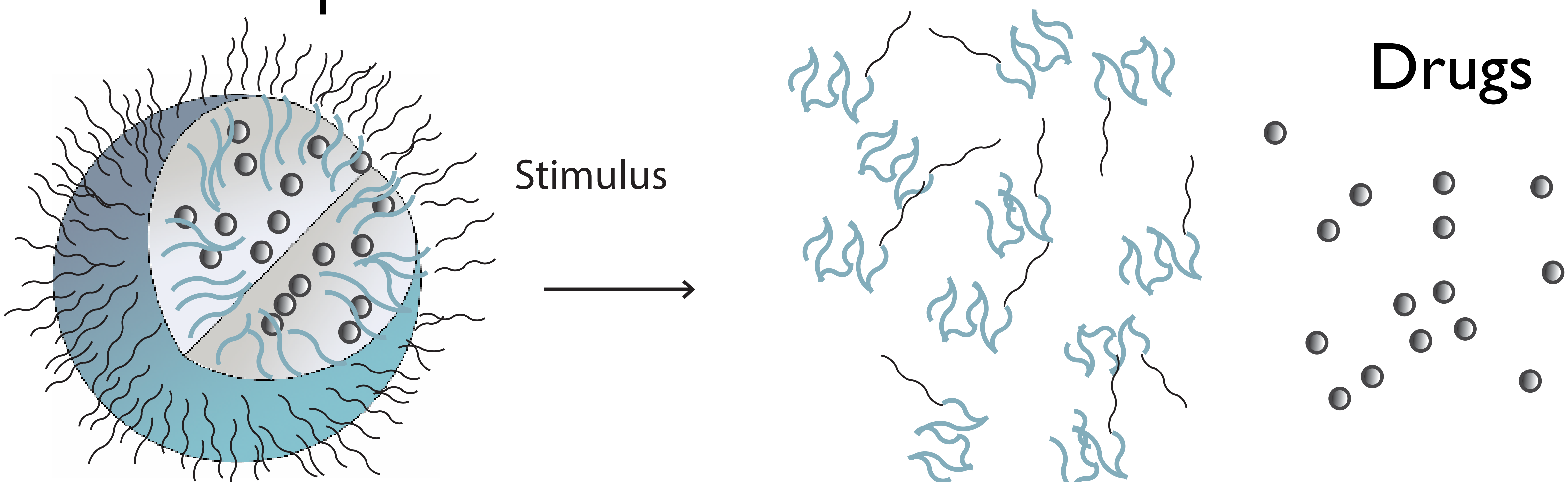
Polymers as nano-capsules for drug delivery

Responsive polymers:

E.g. thermoresponsive poly (N-isopropyl acryl amide) PNIPAAM



stimuli-responsive micelles:



Summary

- **polymers are long chain-like molecules**:
Some key words: connectivity, entanglements, slow dynamics, high viscosity

- Polymers provide **flexibility, elasticity, strength, light-weight**

- **Polymers can make nanomaterials through self-assembly**- precise size and shape. Nanolitography masks, nanofilters etc.

- **Nanocomposites are dispersed nanoparticles in polymer matrices**: flexible, strong lightweight materials. Photovoltaics, photonic crystals, tunable optical and electronic properties

- Polymer materials can be used for **drug delivery and tissue engineering**