Variety of Polymeric Materials [pln45]

Synthesis, architecture, and attributes:

- Polymers are macromolecules of covalently bonded repeat units (monomers).
- The repeat units may be assembled uniformly, periodically (alternatingly), or aperiodically. In stereochemistry such arrangments are named *isotactic*, *syndiotactic*, and *atactic*, respectively. Polymers with single (multiple) repeat unit are called *homopolymers* (*copolymers*).
- Synthetic polymers include glues, fibres, resins, and rubbers. They are assembled industrially via *polymerization* from monomers or via *polycondensation* from shorter polymers.
- Biopolymers include nucleic acids, proteins, and sugars. They are assembled organically.
- Most synthetic polymers are carbon based.
- Aperiodic polymers may
  - manifest quenched disorder (in industrial synthesis),
  - carry information on structural/functional units (in DNA),
  - carry building blocks for structural/functional units to be self-assembled via folding (in proteins).
- Polymers may be linear or branched. Branching strongly affects rheology. Branching is a manifestation of quenched disorder.
- *Degree of polymerization*: numbers N of monomeric repeat units. Monodisperse polymers have the same N and polydisperse polymers a distribution of N.
- *Entanglement* of polymers produces viscoelasticity. Branching suppresses (viscous) flow and enhances elasticity.
- *Block copolymers* have repeat units with different chemical attributes arranged in blocks. They can be designed for self-assembly into nanostructures via micro-phase separation.
- Polymer macrostates:
  - *liquid*: melt, solution, very viscous or viscoelastic,
  - *glass*: amorphous, solid-like,
  - *semi-crystalline*: small crystals embedded in amorphous matrix,
  - *liquid crystalline*: liquid with (mostly) orientational order.
- Bonds too weak for a stable gas except at at low temperature under very low pressure. Dilute polymer solution is effectively a gas state.

- Polymer classification dominated by rheology (rich solution behavior).
- Distinguish between
  - *configurations:* electronic structure of monomers and bonds,
  - *conformations:* spatial arrangements and motion of monomers.

  Statistical physics of macromolecules is concerned with conformations.
- Long-range correlations:
  - high susceptibility to external forces and strong fluctuation effects are linked by fluctuation-dissipation relation,
  - bonds between monomers suppress entropy.
- Memory effects:
  - memory of formation conditions,
  - memory of previous motion,
  - topological memory (exclusion of crossings).
- Entropic nature of elasticity:
  - stretching constrains available conformations.
- Miscibility of polymers dominated by enthalpic term in free energy. Polymers have small entropy of mixing. Phase separation caused by very small repulsive force.
- Fibres:
  - Cell walls in plants contain the biopolymer *cellulose*.
  - Fibres harvested from diversity of plants: cotton, flax, hemp,...
  - Fabrics woven with polymer fibres.
  - Wool made from protein *keratin*.
  - Silk contains biopolymer *fibrion*.
  - Fibres from synthetic polymers: *polyamides*, *polyesters* (e.g. nylon), *polyacrylics*.
  - Useful fibres have high tensile strength, are pliable, and resist abrasion.
  - Fibres are spun in different ways, synthetic fibres mostly from solution or melt.
  - Polymer fibres can be stengthened by a process of drawing (stretching out).