School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials

Polymer Science 2025/26

Summary of what you need to know for the Exam

meaning of red, bold: there is an associated equation (at the end of the document) that you must know by heart.

1. **Synthesis methods**: Overview of the most important polymers: thermoplastics, elastomers, thermosets. Principle differences between step-growth and chain-growth polymerizations. **Why high conversions are needed in step growth polymerizations (polycondensation, polyaddition)?** Particularities of radical (termination modes, gel effect, glass effect). Particularities of living ionic and insertion polymerization. Examples for polycondensation (PET, polyamides), polyaddition (polyurethanes - *what happens in the presence of water*?), and crosslinking (natural rubber). Reaction types for the *Big* 5 (HDPE, LDPE, iPP, aPS, PVC). Typical routes for most technical polymers (PC, PET, PEEK etc.).

2. **Chemical structure**: definitions (monomer, repeat unit, etc.). Difference between conformation and configuration. Types of isomerism (head-tail, *cis*-*trans*, tacticity). Chain architectures and different types of copolymers. Influence of configuration on physical properties (examples: polyisoprene, polypropylene).

3. **Molar mass and dispersity**: know and apply **formulas for M_w, M_n and Đ**. Why M_w often correlates better with physical properties than M_n. Methods to determine molar mass and distribution. Expected molar mass distribution for polycondensates, classical radical polymerization, living polymerization. Understand that kinetics control the distribution. Consequences of molar mass and dispersity for physical properties. Practical considerations: Do we want the highest M_w? Is a dispersity close to 1 always desirable?

4. **Conformations of a macromolecule**: "size" of a freely jointed chain. **Formula for the root-mean-square distance R_n and how it is derived?** Meaning of a Gaussian chain. Radius of gyration. More realistic models for R_n; concept of chain rigidity, C_∞, and factors influencing it. Kuhn segments. Real chain behavior: excluded volume, theta conditions. Be able to estimate R_n from simple calculations. Judge if one polymer is stiffer than another based on chemical structure.

5. **Macromolecules in the condensed state**: origin of cohesive forces in polymers. Typical bond strengths. Cohesive energy: meaning and link to physical properties (e.g. compression modulus K). Why polymers cannot be evaporated by heating. Solubility parameter: definition, how determined for polymers. Links between solubility, cohesive energy, compressive modulus K, and interaction parameter χ.

6. **Glass transition**: definition of a glass; definition of the amorphous state. Chain conformation in the glassy state. Glass transition temperature T_g: definition and significance. Measurement methods (specific volume, heat capacity, mechanical properties – plot of $E(T)$ with correct orders of magnitude in different regimes, dynamic measurements). Influence of molar mass M and temperature T. Influence of measurement speed. Free volume theory (definition of free volume; what happens at T_g?). Relation between T_g and structure: effect of chain stiffness (bulky groups), specific interactions, molar mass, branching, internal and external plasticization, copolymerization. Be able to predict whether a given structure or modification will increase or decrease T_g.

7. **Single crystals and semicrystalline polymers**: which polymers crystallize? Criteria for crystallinity (regularity, tacticity, chain symmetry) and representative examples. Chain folding and lamellar crystals: basic concept of polymer single crystals; folded-chain lamellae vs. extended-chain crystals. Melting behavior: definition of T_m and equilibrium melting temperature T_mo. **Thomson-Gibbs equation** (qualitative and quantitative understanding: why $T_\mathrm{m} << T_\mathrm{mo}$, and how T_m depends on lamellar thickness, l). Kinetics effects on the apparent T_m: critical lamellar thickness and nucleation barrier (conceptual understanding of their dependence on surface free energies and degree of supercooling). Dependence of T_mo on thermodynamic quantities (melting enthalpy and entropy). Influence of chain rigidity and specific interactions (with examples). *You should be able to assess whether a given structure can crystallize and whether it will have a relatively high or low* T_{mo}.

8. **Structures of semicrystalline polymers**: Concept: distinction between amorphous and crystalline regions, typical degrees of crystallinity. Morphology and hierarchical structure (lamellae, stacks, spherulites). Spherulitic growth (mechanism, giant dislocation, multiplication, et.). Specific examples: iPP, PE (including crystal structure), comparison between HDPE, LDPE, and UHMWPE (role of branches, entanglements, and molar mass), polyamides, etc. Oriented polymers: how drawing and orientation affect crystallization, morphology, and mechanical properties. *You should be able to interpret and provide schematic sketches, recognize the hierarchical structure of semicrystalline polymers, and discuss how processing (cooling rate, stretching) affects morphology and properties.*

9. **Rubbery elasticity**: what is that and what are necessary conditions for it to occur? Understand the physical origin of rubber elasticity and the behavior observed when T varies on application of a large constant strain, understand why an elastomer can usually be considered to be incompressible, understand the statistical model for elastomers and its limitations (you don't have to learn it by heart, but understand the principles of the calculations, the main results and the meaning of the different terms). **Formula for the Young's modulus of an elastomeric network, given the number of crosslinks/volume and the temperature in K**.

10. **Linear Viscoelasticity**: What is it and how important is it? Sketches of the behavior of a solid (amorphous) polymer as a function of time (creep, relaxation, simple tension), Boltzmann's principle and its application, principle of dynamic mechanical analysis, definition of loss and storage moduli and of the loss factor, complex notation, understand how one can use a very simple phenomenological model (Maxwell) to obtain a relaxation modulus, the use of Boltzmann's principle to obtain the loss and storage moduli and the loss factor as a function of frequency; how can we approximate the behavior of a real system with this type of model; understand the notion of time-temperature equivalence and how we can use time-temperature superposition to extend the timescale or frequency of a measurement in the linear domain, as well as the limitations of this approach; notions of nonlinear viscoelasticity.

11. **Molecular models for viscoelasticity**: physical basis of Rouse's model for the dynamics of an isolated chain, why doesn't this model work for an isolated chain in a solvent, but is valid for a polymer chain in the molten state if $M < M_e$, physical origin of entanglement, interpretation of the rubbery plateau in an non-crosslinked amorphous polymer. ***You should be able to estimate the Young's modulus corresponding to the rubbery plateau of an amorphous polymer for a given entanglement density or entanglement molecular weight, M_e*** (it is useful to remember that the density of a polymer is always close to 1 g/cc). Concept of critical molar mass, M_c. Which polymers have the lowest/highest entanglement densities? Origin of the transition to viscous behavior (tube model, relaxation according to the tube model), **dependence of reptation time and viscosity on M**. Be able to sketch the $E(T)$ diagram (or $E(\log t)$ or $E(\log \omega)$ for an amorphous, a crosslinked amorphous polymer or a semi-crystalline polymer.

12. **Phenomenology of the plasticity of polymers**: stress-strain curve for a ductile polymer and a brittle polymer, differences with metals, definition of the yield point, σ_y, orders of magnitude of σ_y in polymers, origin of necking during a tensile test on a ductile polymer, meaning of λ_{max} and its link with rubber elasticity. ***Be able to estimate λ_{max} from M_e or the Young's modulus of the rubbery plateau***. Dependence of the yield strength with pressure, T, and strain rate; Eyring model and its limitations (example of

PC, PVC), importance of secondary transitions (example of TMPC). Notions of the differences between the behavior of amorphous and semi-crystalline polymers (importance of l and the degree of crystallinity for σ_y).

13. **Crazes and rupture**: description of a craze in an amorphous polymer, the conditions under which it is observed and its consequences, surface stretching model and the link between the crazing stress at a given speed and the surface energy, understand why polymers with a low entanglement density form crazes more easily than polymers with a high density of entanglements; crazes and disentanglement (under which conditions? Influence of T, strain rate and M), tensile strength as a function of the entanglement density and M, understand highly crosslinked polymers are usually brittle.
14. **Polymer Mixtures**: origin and meaning of the terms in the Flory-Huggins equation, in particular the interaction parameter and its relation to the solubility parameter. Why are most polymers immiscible? Examples of miscible systems (PS/PPO, PVC/PCL) and why they are miscible. Phase diagrams and phase separation mechanisms (definitions of spinodal, binodal, spinodal decomposition, nucleation and growth). Influence of a flow on the morphology of an immiscible system and its practical importance. Other methods of controlling the morphology, importance and function of stabilizers ("emulsifiers") and reactive systems. Morphologies of block copolymers. Examples and applications.
15. **Major polymer classes and polymer processing**: chemical structures of the major polymer families (PE, PP, PS, etc.), their material's structure, resulting thermal and mechanical properties. Understand the links to previous chapters. Principle steps of extrusion and injection molding. Influence of flow on final product performance.

16. **Formulas you should know** (highlighted in red above).

Carothers equation for equal stoichiometry:

$$\bar{X}_n = \frac{1}{1-p}$$

Root-mean-square distance between the ends of a linear chain in its statistical conformation and the corresponding radius of gyration:

$$R_n = \sqrt{C_\infty n}a \qquad R_g = \frac{R_n}{\sqrt{6}}$$

Different average molecular weights and dispersity:

$$M_n = \sum_{i=1}^{\infty} n_i M_i \Big/ \sum_{i=1}^{\infty} n_i = \sum_{i=1}^{\infty} i n_i M_o \Big/ \sum_{i=1}^{\infty} n_i$$

$$M_w = \sum_{i=1}^{\infty} w_i M_i \Big/ \sum_{i=1}^{\infty} w_i = \sum_{i=1}^{\infty} n_i M_i^2 \Big/ \sum_{i=1}^{\infty} n_i M_i = \sum_{i=1}^{\infty} i^2 n_i M_o \Big/ \sum_{i=1}^{\infty} i n_i$$

$$Đ = \frac{M_w}{M_n}$$

Thomson-Gibbs equation:

$$T_\mathrm{m} = T_\mathrm{m0}\left(1 - \frac{2\sigma_\mathrm{e}}{\Delta h_v \cdot l}\right)$$

Young's modulus (and shear modulus, equation not shown here) of an elastomer at $T > T_\mathrm{g}$ (ignoring entanglement):

$$E = \frac{\sigma}{\varepsilon} = 3NkT$$

The modulus (and shear modulus, equation not shown here) of the rubbery plateau of an entangled thermoplastic polymer:

Relation between entanglement density, entanglement molecular weight, and plateau modulus of the rubbery state:

$$M_e = \frac{N_A \rho}{N_e} = \frac{3 N_A k T \rho}{E_e} \equiv \frac{3RT\rho}{E_e}$$

Definition of the critical molecular weight:

$$M_c = 2M_e$$

Molar mass dependence of the reptation time (disentanglement time):

$$\tau_d \propto M^3$$

Dependence of the viscosity of a polymer on molar mass:

$$\eta \sim \left(\frac{M}{M_e}\right)^3 ; \quad M > M_c \equiv 2M_e$$

$$\eta \sim \frac{M}{M_e}; \quad M \leq M_c \equiv 2M_e$$