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

Polymer Science 2024/25

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 should be known by heart.

1. **Chemical structure**: definitions (monomer etc.), difference between conformation and configuration, different types of isomerism (head-tail etc., *cis*-*trans*, tacticity), architectures, different types of copolymers. What is the influence of these different configurations on the physical properties (examples of polyisoprene, polypropylene)?

2. **Molar mass and dispersity**: know the **formulas for M_w, M_n and Đ** and why M_w is often more representative of the physical properties than M_n. How can these quantities be determined? What is the expected molar mass distribution for a polycondensate, a classical radical polymerization, a living polymerization? Understand that kinetic factors are decisive for the molar mass distribution. What are the consequences for the physical properties? Do we always want M_w to be as high as possible? Do we want a dispersity close to 1 or rather high in practice?

3. **Conformations of a macromolecule**: the "size" of a freely jointed molecule, **formula for the root-mean-square distance between chain ends, R_n. How is it derived?** What is meant by a “Gaussian chain”? Radius of gyration; more realistic models for R_n, notion of the rigidity of a chain, C_∞, and the factors that influence it; Kuhn segments. Real polymer chain behavior, excluded volume, theta conditions. *You must be able to estimate R_n from simple calculations! You must be able to decide if one polymer is stiffer than another based on their chemical structures.*

4. **Macromolecules in the condensed state**: origin of cohesive forces in polymers, typical bond strengths, meaning of cohesive energy and its link with physical properties, in particular compression modulus, K. Why can’t we evaporate a polymer by heating it? Solubility parameter (what is it and how can it be determined for a polymer?), link between solubility, cohesive energy, compressive modulus, K, and interaction parameter χ.

5. **Glass transition**: definition of a glass, definition of the amorphous state, conformation of chains in the glassy state, glass transition temperature (what is it?), T_g measurement methods (specific volume, heat capacity, mechanical properties – plot of E(T) for an amorphous polymer with correct orders of magnitude in the different temperature regimes, indication of the influence of M and T, dynamic measurements), influence of the measurement speed, free volume theory (what is free volume? What happens at T_g according to this theory?), relation between T_g and structure: influence of stiffness (bulky groups), specific interactions, effect of molar mass, branching, internal and external plasticization, copolymerization. *You must be able to tell, if a given structure or a given structural modification will lead to a higher or lower* T_g.

6. **Structures of semi-crystalline polymers**: polymers that crystallize (criteria, examples), importance of tacticity, dependence of T_{mo} on melting enthalpy and melting entropy, influence of kinetics on the apparent T_m, importance of rigidity, 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 relatively low* T_{mo}.

7. **Single crystals and semi-crystalline polymers**: folding of chains, T_m of a lamella (why $T_m << T_{mo}$, and how T_m varies with the lamella thickness, l), notions of semi-crystalline polymers, structure of a spherulite, mechanism of spherulitic growth (giant dislocation, multiplication of lamellae, etc.), peculiarities of the structure of iPP, peculiarities of different PE grades (including its crystal structure), oriented polymers (morphology, influence of orientation on crystallization), UHMWPE.

8. **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**.

9. **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.

10. **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.
11. **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).
12. **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.
13. **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.

14. **Synthesis methods**: Overview of the most important polymers, thermoplastics, elastomers and thermosets. Principle differences between step-growth and chain-growth polymerizations. **Why are high conversions needed in step growth polymerizations (polycondensation or polyaddition)?** Particularities of radical (for example, termination modes, chain transfer, gel effect, glass effect), (living) ionic and insertion polymerization. Examples of polycondensation (PET, polyamide), polyaddition (polyurethane - but what happens in the presence of water?), and crosslinking (natural rubber). Which reaction type is used for the *Big* 5 (HDPE, LDPE, iPP, aPS, PVC)? What about most technical polymers (PC, PET, PEEK etc.)?

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:

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

Different average molecular weights and dispersity:

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

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

$$Đ = \frac{M_w}{M_n}$$

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:

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

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:

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

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