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

Polymer Science Written Exam,

Friday 22.01.2025 from 9:15 to 12:15 (3 hours), Room CE1101

First name: .... **Surname:** ....

a) With the exception of the A4 sheets distributed, you are not entitled to any documents (course notes, books, etc.). **Calculators, computers, mobile phones and other electronic media are not allowed**.

b) The exam consists of 12 multiple-choice questions and six long questions. **A list of common polymers and some of their basic properties is also given at the end of the exam paper, along with additional useful information.**

c) Each multiple-choice question is worth 2 points for a correct answer and 0 points for a wrong answer or no answer at all. There is only one correct answer to each question among those proposed. **You should therefore answer *all* the multiple-choice questions and tick only one box per question.**

d) The long questions are worth 12 points each for a perfect answer. **You should try to answer *four* (4) long questions out of the *six* proposed**.

Multiple-Choice Questions

1. Which of the following statements about polymer chain conformations is *correct*?
   a) The "freely rotating chain" model allows for greater flexibility than the "freely jointed chain" model, resulting in a smaller end-to-end distance, R_n, for a given chain length n. ☐
   b) Flory´s characteristic ratio C_∞ quantifies the deviation of a real polymer chain from the ideal chain model and is defined as the ratio of the actual bond length to the bond length of a fully extended, infinitely stiff polymer chain. ☐
   c) The size of a polymer chain, represented by the root mean square end-to-end distance, R_n, depends on the bond length, l, and the number of bonds in the chain, n, and it scales as $n^{1/2}$. ☑
   d) For a freely jointed chain, the radius of gyration, R_g, is always larger than the root mean square end-to-end distance, R_n, regardless of chain length. ☐

2. Which factor most strongly affects the glass transition temperature (T_g) of a polymer blend?
   a) The relative amounts of amorphous and crystalline phases in the blend. ☐
   b) The molecular weight distribution and dispersity of the blend components. ☐
   c) The immiscibility of the polymer components, which determines phase separation in the blend. ☐
   d) The temperature at which the polymer was processed and the rate of cooling from the melt. ☑

3. A polymer sample consists of 10 chains with a molar mass of 8’000 g/mol, 5 chains with a molar mass of 10’000 g/mol, and 2 chains with a molar mass of 15’000 g/mol. What is the dispersity of this sample?
   a) 1.1 ☐
   b) 1.5 ☐

c) 2.0 ☒
d) 5.0 ☐

4. Which of the following statements is *false*?

a) A key advantage of using block copolymers in material applications is that they combine the properties of different polymers in one material, such as rubbery and glassy domains. ☐
b) Polymers are semi-crystalline due to the equilibrium between crystalline and amorphous phases. ☒
c) The onset of plastic deformation in polymers is influenced by entanglements, which stabilize large strains and contribute to ductility. ☐
d) According to the Boltzmann superposition principle, the incremental response of a material to stress depends on both the current and the past stresses experienced by the material. ☐

5. Estimate the critical molecular weight, M_c, for a polymer with a density of 0.92 g/cm^3 and an entanglement density of 4 x 10^{25} chains/m^3.

a) 13800 g/mol ☐
b) 27600 g/mol ☒
c) 41400 g/mol ☐
d) 55200 g/mol ☐

You don't need a calculator for estimating the entanglement molar mass:

$$M_\mathrm{e} = \frac{\mathrm{N_A}\rho}{N_\mathrm{e}} = \frac{6\cdot 10^{23}\,\frac{1}{\mathrm{mol}}\cdot 0.92\,\frac{\mathrm{g}}{\mathrm{cm}^3}}{4\cdot 10^{19}\,\frac{1}{\mathrm{cm}^3}} = 1.38\cdot 10^4\,\frac{\mathrm{g}}{\mathrm{mol}}\quad .$$

The critical molar mass is then twice M_e.

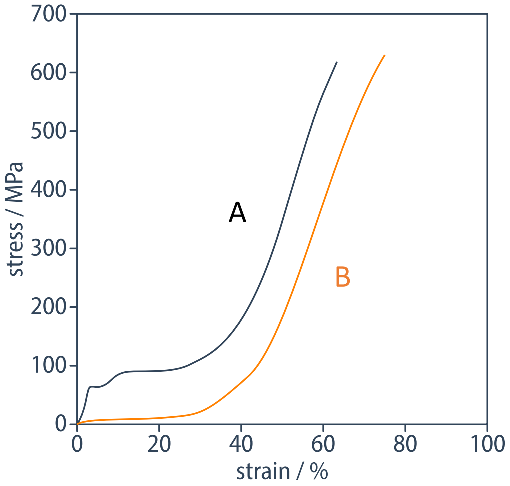
Long Questions

Question 2.

PET is a thermoplastic polyester widely used in packaging, textiles, and engineering applications due to its excellent strength, chemical resistance, and thermal stability. Its properties can vary significantly depending on the processing history.

How is PET synthesized industrially? (**1 pt**)

See Slide 446. Polycondensation of terephthalic acid (or dimethyl terephthalate) and ethylene glycol. First, bis(hydroxyethyl) terephthalate is formed that undergoes polymerization at elevated temperatures and reduced pressure for removal of ethylene glycol condensation byproduct.



The Figure shows two stress-strain curves of PET, recorded at 25 °C and 100 °C after different thermal and processing histories. Explain why the stress-strain behavior differs between Curve A and Curve B, considering structural differences of the two materials. (**3 pt**)

See Slide 447.

Curve A represents semicrystalline PET, obtained by slower cooling or controlled processing such as stretching. Semicrystalline PET is stiffer and stronger due to the presence of crystalline domains (at reduced ductility).

Curve B represents amorphous PET, obtained by rapid cooling (quenching). Amorphous PET becomes significantly soft, when heated above its T_g at around 70 °C, and shows a low strength until strain-hardening occurs.

Draw schematically the evolution of the specific volume as a function of temperature for the two processes that lead to type A and type B. (**2 pt**)

For specific volume-temperature plots during glass transition (smaller slope below the glass transition temperature) and crystallization (discontinuous drop of specific volume at the crystallization temperature), see Slides 143 and 145.

During a differential scanning calorimetry (DSC) experiment, an enthalpy overshoot is often observed during heating following rapid cooling. Explain the origin of this overshoot and how it relates to physical aging. (**3 pt**)

See Slides 147 and Exercise Sheet 4. Rapid cooling below T_g traps the polymer chains in a non-equilibrium state, but over time the chains rearrange toward a lower-energy state, increasing density and reducing free volume. Upon reheating, the polymer must absorb extra energy to return to equilibrium, causing the observed overshoot.

Physical aging reflects the slow densification of amorphous regions below T_g, which increases brittleness and stiffness over time.

Explain how the difference in processing history is utilized in the fabrication of PET bottles. In your answer, describe the principal steps of the bottle blow-molding process and comment on the relevance of strain-hardening. (**3 pt**)

See Slides 447 and 448. An amorphous preform is heated to above the glass transition temperature and stretch blow-molded into the bottle shape. During stretching, the polymer chains align and partially crystallize, resulting in strain-hardening. This ensures uniform material distribution and enhances mechanical properties such as tensile strength and impact resistance.

Question 2.

Nylons are a class of polyamides widely used due to their excellent mechanical and thermal properties. Their performance is strongly influenced by their molecular structure and the microstructure that develops during processing.

Draw the chemical structure of Nylon-6,6 and explain how its molecular structure facilitates and influences crystallization. (**2 pt**)

See Exercise 5 for the chemical structure of Nylon-6,6. For factors influencing crystallization and the melting temperature, see Slides 186-192.

Regular chain architecture enables polymer crystallization. The amide (-CONH-) groups in the polymer backbone form hydrogen bonds that promote chain alignment and facilitate crystallization by contributing to the favorable enthalpy change of crystallization

Describe the typical morphology (microstructure) observed in nylons that are cooled from their melt. (**2 pt**)

For the spherulite structure and origin, see Slides 195-197. Spherulites are more or less spherical clusters of amorphous materials and crystalline matter. They contain lamellae, separated by amorphous layers, that are arranged radially, oriented along the radii of the spherulites, giving the spherulite its characteristic morphology.

Explain why the lamellar thickness of nylon crystals is typically limited to nanometer dimensions. (**3 pt**)

For the determination of lamellar thicknesses by crystallization kinetics, see Slides 181-183 and the corresponding Reader. At typical cooling rates, crystallization is governed by kinetically driven nucleation and growth, which proceeds much faster than the formation of fully extended chain crystals. The formation of the latter would require an infinitely high energy barrier and an infinite amount of time. Consequently, polymer chains fold back and forth within the crystalline regions, resulting in lamellae thicknesses on the order of 10 nm to form at a practical rate at typical cooling rates.

What are possible consequences of limited lamellar thickness on the mechanical and thermal properties of Nylon-6,6? (**2 pt**)

See Slides 182 and 337-339, corresponding Lecture Notes, as well as Exercise Sheet 5. The melting point and yield strength decrease as lamellar thickness decreases.

Nylon-6,6 is commonly used in fibers. Discuss how the fiber spinning process impacts crystallinity and morphology in Nylon-6,6 fibers. Explain how these processing-induced changes affect the mechanical properties, such as tensile strength and elongation at break along the fiber direction. (**2 pt**)

For the effect of orientation on melting temperature and morphology, see Slides 187 and 199. During fiber spinning, the polymer chains are stretched and oriented along the fiber axis, enhancing crystallinity and inducing an oriented shish-kebab structure. Increased crystallinity and molecular orientation improve tensile strength. However, increased alignment reduces the ability of chains to deform plastically, leading to lower elongation at break.

Nylons often absorb moisture from the environment. Although this does not necessarily directly influence the crystal structure, explain in which way moisture can affect their mechanical properties. (**1 pt**)

For the plasticization of nylons by water, see Slide 156. Water acts as a plasticizer by competing with the polymer chains for hydrogen bonding interactions. This lowers the T_g, making the polymer more flexible and less rigid, and can result in reduced tensile strength and stiffness.

Useful Information:

Avogadro's number: $N_A = 6.022 \times 10^{-23}$ mol^{-1}

Boltzmann's constant: $k_B = 1.38$ x 10^{-23} J K^{-1}

universal gas constant: $R = 8.314$ J K^{-1} mol^{-1}

bond length of a carbon-carbon single bond: 1.54 Å

bond length of a carbon-oxygen single bond: 1.43 Å

The WLF equation: $\log a_T = -\frac{C_1(T-T_g)}{C_2+T-T_g}$, with $C_1 = 17.5$ and $C_2 = 51.6$

Table 1. Characteristic properties of selected polymer materials.

material	entanglement density [mmol/cm³]	entanglement molar mass, M_e [g/mol]	T_g [°C]	T_m [°C]	C_∞
polybutadiene		1'900	-85		5.8
poly(methyl methacrylate) (PMMA)	0.127	9'000	105		8.2
polyamide 66 (PA 66, nylon 66)	0.537	2'000	55	264	6.1
polyamide 6 (PA 6, nylon 6)	0.435	2'500	50	220	6.2
Kevlar			123	> 500	> 300
poly(ethylene terephthalate) (PET)	0.815	1'600	70	260	4.2
polycarbonate (PC)	0.725	1'800	147	265	2.4
polyvinyl acetate		3'750	38		9
isotactic polypropylene (iPP)		5'800	-10	160	5.9
atactic polystyrene (PS)	0.0561	19'000	100		10.8
low-density polyethylene (LDPE)	0.613	1'400	-100	110	6.8
high-density polyethylene (HDPE)	0.613	1'400	-110	130	6.8
polyoxymethylene (POM)		2'200	-80	165	7.5
polyethylene oxide (PEO)		1'700	-50	69	6.7
polytetrafluoroethylene (PTFE)		5'400	120	327	10-15
polyvinylchloride (PVC)	0.252	5'600	82		7.6