EPFL

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 ☐

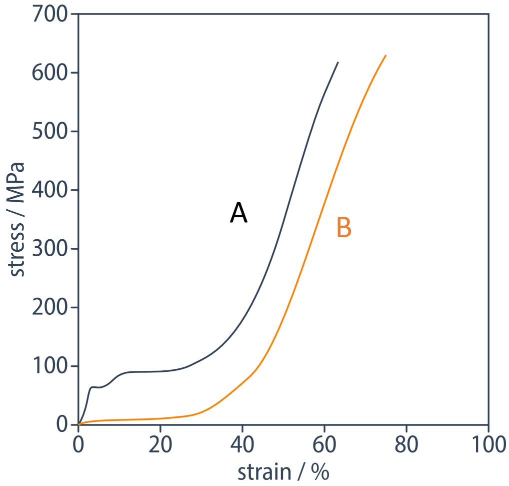
Dr. Daniel Görl
daniel.gorl@epfl.ch
lmom.epfl.ch

EPFL STI IMX LMOM
MXG 136, Station 12
CH-1015 Lausanne

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**)

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**)

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**)

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**)

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**)

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**)

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

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

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

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**)

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

Useful Information:

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

Boltzmann's constant: $k_B = 1.38 \times 10^{-23}$ 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/cm^3]	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

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