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

Polymer Science Written Exam,

Friday 02.02.2024 from 9:15 to 12:15 (3 hours), Room CE12

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

3. Which material is capable of nearly full recovery of its original shape after tensile deformation at room temperature using a strain of 20%, i.e. deformation to well beyond the yield strain?

a) polymethyl methacrylate (M_n = 120’000 g/mol) after heating to 150 °C. ☐

b) polystyrene (M_n = 20’000 g/mol) after heating to 150 °C. ☐

c) poly(ethylene terephthalate) (M_n = 120’000 g/mol) after heating to 50 °C . ☐

d) None of them because plastic deformation is generally irreversible. ☐

4. Which is *false*?

a) The glass transition temperature, T_g, of miscible polymer blends may be modified by adjusting the composition of the mixture. ☐

b) Block copolymers comprising immiscible blocks of one soft, rubbery polymer and one hard, glassy polymer tend to show two distinct T_g’s. ☐

c) Thermoplastic elastomers are usually based on blends of an elastomer with a glassy or semicrystalline polymer. ☐

d) The addition of small elastomeric particles to a glassy polymer matrix by mixing or by copolymerization is a way to improve the impact resistance of brittle polymers. ☐

5. Estimate the weight-average molar mass, M_w, of a polypropylene sample with dispersity of 7, if 5×10^{-19} g of this sample are composed of 50 macromolecular chains.

a) 35’000 g/mol ☐

b) 42’000 g/mol ☐

c) 50’000 g/mol ☐

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

EPFL STI IMX LMOM
Dr. Daniel Görl
daniel.gorl@epfl.ch
+41 21 693 78 65

EPFL STI IMX LMOM
Dr. Christopher Plummer
christopher.plummer@epfl.ch
+41 21 693 10 05

d) 75’000 g/mol ☐

7. What is meant by “excluded volume”?

a) the volume that is inaccessible to the segments of a real polymer due to a self-avoidance condition in the chain random-walk, which results from the repulsive part of the effective interaction potential for the repeat units. ☐
b) the volume that is not occupied by the polymer due to the self-overlapping random walk of the polymer chain segments. ☐
c) the volume that is not occupied by the poylmer due to the ideal random walk of the polymer chain segments. ☐
d) the volume that results from the sum of the volume of all repeat units of the polymer chain. ☐

9. Which of the following polymers is best suited to thermoforming?

a) poly(methyl methacrylate) (PMMA) ☐
b) nylon 6 ☐
c) Kevlar ☐
d) polyoxymethylene (POM) ☐

12. Which is the best description of high-density polyethylene (HDPE)?

a) HDPE is usually synthesized by free radical polymerization of highly compressed ethylene gas at temperatures above the polyethylene melting temperature. ☐
b) Because of its low degree of branching and high crystallinity, the Young’s modulus of HDPE is even higher than that of the engineering polymer polyoxymethylene (POM). ☐
c) In its most stable crystalline form, the HDPE chains adopt the enthalpically most favored *zig-zag* conformation in a hexagonal unit cell. ☐
d) HDPE has a higher maximum use temperature than low-density polyethylene (LDPE) because it has a higher melting temperature (around 130 °C), primarily determined by London dispersion interactions between the polymer chains. ☐

EPFL STI IMX LMOM
Dr. Daniel Görl
daniel.gorl@epfl.ch
+41 21 693 78 65

EPFL STI IMX LMOM
Dr. Christopher Plummer
christopher.plummer@epfl.ch
+41 21 693 10 05

Long Questions

Question 1.

You are supposed to synthesize a poly(butadiene-*b*-styrene) block copolymer with a well-defined periodic lamellar morphology. Propose a plausible and detailed reaction mechanism including all essential steps, starting materials, and reagents. (**5 pt**)

How can you control the molecular weight for each block? (**1 pt**)

Comment on the molecular weight distribution and the expected dispersity. (**1 pt**)

How is it possible to obtain an analogous ABA-triblock copolymer with an internal polybutadiene block comprising 75 wt% of the total polymer mass? (**1 pt**)

Sketch the Young's modulus as a function of temperature for this triblock copolymer including the correct orders of magnitude and an assignment of the different temperature regimes. (**3 pt**)

How can you improve the creep resistance of this triblock copolymer at high temperatures? (**1 pt**)

Question 4.

For a viscoelastic material obeying the superposition principle of Boltzmann, schematically depict the evolution of strain $\varepsilon(t)$ over time for a creep experiment in tension, when a stress interval $\Delta\sigma_1$ is applied at a time t_1, a second stress interval $\Delta\sigma_2$ at a time t_2, and a third stress interval $\Delta\sigma_3$ at a time t_3. Hence, explain the origin of the expression

$$\varepsilon(t) = \int_{-\infty}^{t} \mathrm{D}(t-\xi)\frac{\Delta\sigma}{d\xi}\mathrm{d}\xi \ ,$$

where $\mathrm{D}(t)$ is the tensile compliance. (**2 pt**)

For modelling the creep behavior of the material, use a Voigt element composed of a spring and a dashpot that are parallel to another and show that

$$\mathrm{D}(t) = \frac{1}{E}\left(1 - e^{-t/\tau}\right) \ ,$$

where τ is the ratio of the dashpot viscosity, η, and the elastic spring constant, E. You may need the solution for the differential equation $y'(x) + \frac{a}{b}y(x) - \frac{c}{b} = 0$, which can be found at the end of the exam. (**3 pt**)

How does the Voigt model behave under creep within the limits of $t \ll \tau$ and $t \gg \tau$? Plot your results in a strain-time diagram and discuss limitations of the Voigt element to model the viscoelastic behavior of a real polymer! (**5 pt**)

How would you construct a more realistic spring- and dashpot-based model to reproduce the viscoelastic behavior of polymers? (**2 pt**)

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

EPFL STI IMX LMOM
Dr. Daniel Görl
daniel.gorl@epfl.ch
+41 21 693 78 65

EPFL STI IMX LMOM
Dr. Christopher Plummer
christopher.plummer@epfl.ch
+41 21 693 10 05

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 differential equation $y'(x) + \frac{a}{b}y(x) - \frac{c}{b} = 0$ has the solution $y = \frac{c}{a}\left[1 - \exp\left(\frac{-ax}{b}\right)\right]$

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

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

EPFL STI IMX LMOM
Dr. Daniel Görl
daniel.gorl@epfl.ch
+41 21 693 78 65

EPFL STI IMX LMOM
Dr. Christopher Plummer
christopher.plummer@epfl.ch
+41 21 693 10 05