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 ☐

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. ☑

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**)

A well-defined poly(butadiene-*b*-styrene) block copolymer is most plausibly synthesized by **living anionic polymerization**, which allows precise control over molecular weight, block length, and architecture. Draw the chemical structures and mechanism in your solution (see Slide 56)

Monomers and initiators: styrene, 1,3-butadiene.

Initiator: an organolithium compound, typically *n*-butyllithium (*n*-BuLi)

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

For a living polymerization, the final degree of polymerization is given by the ratio of monomer-to-initiator concentration (Slide 57).

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

The molecular weight distribution for a living polymerization is very narrow, provided that the initiation is fast compared to the propagation, and a Poisson distribution is expected. The dispersity is close to zero.

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**)

An analogous ABA triblock copolymer (PS-*b*-PBd-*b*-PS) can be obtained by bidirectional growth, using a difunctional anionic initiator, the growth of the central polybutadiene block first from both ends, and after reaching 75 wt%, addition of styrene to both living chain ends. (We did not treat this in this year's class)

This yields a symmetric ABA triblock copolymer with a rubbery midblock.

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**)

Indicate the glassy state, rubbery state, melt state with correct tick marks for the respective order of magnitude on the modulus axis and for the glass transition temperature of polybutadiene and PS.

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

Permanent covalent (chemical) crosslinking stabilizes the network even when the PS domains soften near their T_g, which prevents flow and significantly enhances high-temperature mechanical stability.

Question 4.

For a viscoelastic material obeying the superposition principle of Boltzmann, schematically depict the evolution of strain ε(*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 D(*t*) is the tensile compliance. (**2 pt**)

see Slide 261. For a linear viscoelastic material obeying the Boltzmann superposition principle, the total strain $\varepsilon(t)$ at any time *t* is the sum of the individual strain responses caused by each stress increment. Because stress is additive, the strain contribution of each stress increment can be summed. If the applied stress varies continuously with time, the discrete stress steps $\Delta\sigma_i$ are replaced by infinitesimal stress changes, leading to the Boltzmann superposition integral.

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**)

See Exercise 8.

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**)

See Exercise 8: transition between infinitely rigid solid and elastic behavior.

No instantaneous deformation possible, cannot describe stress relaxation. Only a single relaxation time is present. Polymer-specific features such as chain entanglements are not considered.

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

Real polymers exhibit a broad spectrum of relaxation processes. A more realistic description requires multiple relaxation (see Generalized Voigt Model), represented by a relaxation time spectrum.

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