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

Polymer Science 2024/25

Mock Exam – Solutions

In the real exam, you should write your answers on A4 sheets distributed by us. You are not allowed to use any other document (course material, books, etc.). Calculators, computers, mobile telephones, and other electronic media are not permitted.

You should answer all the multiple-choice questions (in the real exam probably 12 questions in total) and 4 out of the 4 - 6 offered longer questions.

Multiple-choice questions

1. Which of the following reactions is a polycondensation?

   a) Reaction of an epoxy resin with a diamine in a closed mold. ☐
   b) Reaction of a diisocyanate with a diol in the presence of water to form a foamed polyurethane. ☑
   c) Ring opening polymerization of caprolactam to form polyamide 6. ☐
   d) Radical polymerization of ethylene to form polyethylene. ☐

   Note: usually, the reaction of a diisocyanate and a diol leads to a urethane without the production of a leaving group, i.e., *polyaddition* as opposed to *polycondensation* (see Slide 380). However, in the presence of water, CO_2 is produced during polymerization, which is therefore a polycondensation reaction (see Slide 459).

2. For an amorphous polymer of high molar mass, $C_\infty = 9$ and the maximum deformability of the entanglement network, $\lambda_{max} = 4$. What is the average number of bonds between two entanglement points?

   a) 20 ☐
   b) 36 ☐
   c) 81 ☐
   d) 144 ☑

   λ_{max} is roughly the ratio of the end-to-end distance of a fully stretched entangled strand to its end-to-end distance prior to deformation. If the bond length is a and the number of bonds between entanglement points is n, we have $\lambda_{max} \approx n \times a/\sqrt{C_\infty n a^2}$, so that $n \approx C_\infty \lambda_{max}^2 = 9 \times 16 = 144$.

3. Which statement is false?
   a) Provided that all functional groups of monomers have reacted, the dispersity of an ideal polycondensate tends towards 2. ☐
   b) In a classical radical polymerization, M_w, and the dispersity, may reach very high values compared with those for a polycondensate. ☐
   c) During a living anionic polymerization, a very slow initiation reaction compared with the propagation rate leads to a dispersity close to 1. ☑
   d) The glass transition temperature is sensitive to molar mass, especially when this latter is low. ☐

For the polydispersity to be low, you need all the chains to start growing at the same time. The initiation rate therefore needs to be very fast compared with the propagation rate.

4. After many years of research, the Polymer Laboratory has succeeded in synthesizing a polymer made up of 3 chains with a molar mass of 100, 100, and 400 kg/mol, respectively. What is the dispersity of this polymer?
   a) 1.5 ☑
   b) 2.0 ☐
   c) 3.0 ☐
   d) 4.5 ☐

Use the formula

$$D = \frac{M_w}{M_n} = \left(\sum iM_i^2/\sum iM_i\right)/\left(\sum iM_i/\sum i\right) =$$
$$((2 \times 100^2 + 400^2)/(2 \times 100 + 400)/((2 \times 100 + 400)/(2 + 1)) = \frac{180000/600}{600/3} = 1.5$$

No need for a calculator!!

Longer questions

1. The melting temperature of a crystalline lamella formed by a polymer is given by

$$T_m = T_{m0}\left(1 - \frac{2\sigma_e}{l\Delta H}\right)$$

a) Explain the meaning of the different terms in this equation with reference to a schematic representation of a lamella, and thus explain its physical origin.

For a schematic representation, see Slide 166 of the class, which you should try to reproduce.

T_{m0} is the thermodynamic melting temperature, where the amorphous phase is in equilibrium with the crystalline phase. ΔH is the melting enthalpy of a perfect crystal.

The chains forming a lamellar crystal are parallel to the thickness, l, which is typically of the order of 10 nm. This means, that the polymer chains, which may exceed 1'000 nm in length in a typical polymer, must fold. This folding is energetically unfavourable, especially if the chain is rigid. Hence the surface energy, σ_e, of the upper and lower face of the lamella is large. The melting temperature of a lamella with thickness l is therefore much lower than the thermodynamic melting temperature because this surface energy represents a negative contribution to the effective enthalpy of crystallization.

b) In a semi-crystalline polymer, the lamellae are organized in the form of spherulites. What is a spherulite and what are the mechanisms that lead to the formation of spherulites from lamellar nuclei within a molten polymer when $T_g < T < T_{mo}$?

A spherulite is a more or less spherical cluster of crystalline lamellae containing around 50 % amorphous material in a typical semicrystalline polymer (some, e.g., POM contain more, others, e.g., PET, contain less depending on the crystallization conditions). The lamellae are typically oriented along the radii of the growing spherulite.

For a model of spherulite growth, see Slide 183. We consider first an isolated lamella that nucleates somewhere in a supercooled molten polymer, i.e., at a temperature lower than T_{m0} but above T_g. The lamella grows by adding chains to its lateral surfaces, while maintaining its thickness. In the surrounding melt, the chains are entangled and in constant motion, and hence exert forces on the lamella, which, in view of its reduced thickness, may easily tear.

The tear will create a giant screw dislocation and new lateral surfaces from which the lamella can undergo spiral growth. The chain segments trapped in the amorphous layers between the resulting stacked lamellar layers prefer a statistical conformation, which leads to a separation of the lamellar layers, so that their trajectories diverge rather than remaining parallel.

Multiple events, i.e., repeated tearing, spiral growth, and lamellar separation, result in the formation of a spherical 3D cluster.

If you are answering this question in an exam, you should try to represent these processes schematically as in the slides.

c) During injection molding, a highly stretched molten polymer comes into contact with the walls of a cold mold. What are the consequences for its morphology? (Assuming that the polymer is able to crystallize.)

Crystallization is favoured if the polymer is oriented and stretched by flow or strain, because the entropy penalty incurred by crystallization is reduced (the chains are already in stretched conformations). This leads to stacking of the lamellae along the stretch direction, as, e.g., at the surface of injection mouldings or in extruded/drawn fibres of conventional polymers. If the deformation is very large, shish-kebab structures may be observed, where lamellae nucleate from a core of extended chain crystals aligned along the stretch direction. *Again, schematics would be useful.*

2. a) What is the glass transition and how can it be measured? For a given polymer, do different measurement techniques give the same value for T_g?

In the molten state, the polymer conformations constantly change, typically at the picosecond timescale. On reducing the temperature, the conformational changes slow down. T_g marks the temperature below which they cease entirely, with the exception of very local conformational changes such as crankshaft motions.

For measurement types, see, e.g., Slide 128. In practice, T_g is defined by the ability of a polymer to modify its conformation on the time-scale of the measurement, which generally detects quantities that reflect the polymer mobility (heat capacity, coefficient of thermal expansion etc.). The measured value of T_g therefore strongly depends on the effective measurement speed, which may be related to a cooling rate or a frequency, depending on the technique.

b) Show schematically the shear modulus, G, as a function of T for an amorphous polymer. Indicate the orders of magnitude of G as well as the influence of M and the measurement speed. Show the behavior of a semi-crystalline polymer and an elastomer on the same graph.

See Slide 132, which shows the temperature-dependence of the Young's modulus, which is generally around 3 times the shear modulus.

c) Briefly explain the principle of free volume theory. How does this theory account for the dependence of T_g on M for linear chains? What is the effect of chain branching on T_g?

We consider a randomly packed system composed of identical rigid balls, representing individual polymer segments, that cannot crystallize. At equilibrium, e.g., after infinitely slow cooling, each of these balls takes up an average volume v_0 at absolute zero temperature, which includes the volume of the ball as well as a certain unoccupied volume (the interstices). An increase of temperature creates thermal vibrations that increase the volume each ball takes up, as reflected by the thermal expansion coefficient, but each ball maintains its mean position relative to its neighbours and the polymer hence maintains its initial conformation.

For a ball, i.e., a polymeric segment to change its position, i.e., for the conformation to change, it needs enough room. It is assumed that at some temperature T_0 characteristic of the material, part of the volume created by thermal vibrations is "free" to redistribute, thus creating holes. If one of these holes exceeds the size of a ball, there may be enough room for the ball to change position. As thermal energy increases above T_0, the entire system can hence begin to adjust its conformations and, given enough time, minimize its energy. We hence enter a liquid-like state, which is characterized by a larger thermal expansion coefficient than in the glassy state. The difference in the volume per ball implied by the thermal expansion coefficients in the liquid and glassy states at a given temperature above T_0 is the "free volume", v_f, and we assume the smaller v_f, the more slowly the chains change their conformations. Hence, the T_g we measure on cooling from the liquid state will not be T_0, but the temperature at which v_f decreases to a critical value such that the chains are no longer able to change their conformations on the timescale of the measurement (cf. part (a)). *You should try to show this schematically on a volume-temperature plot.*

The effect of the molar mass is explained in the notes and on Slide 143. We have an extra free volume associated with the chain ends which means the chains have more mobility at a given temperature than in the absence of the chain ends. Hence if the T_g we measure in a given measurement corresponds to a critical value of the free volume, we'll observe a lower T_g in the presence of the chain ends. You can represent this effect on your *volume-temperature plot* and hence show geometrically that

$$T_g = T_{g\infty} - K/M$$

Obviously a branched chain will have more chain ends than a linear polymer so you might assume more branching leads to a lower T_g, but this may be offset by a reduction in chain mobility at very high degrees of branching (increase in chain rigidity), particularly if the branches are short.

3. a) Explain qualitatively the concept of entanglement, the entanglement network model and the tube model.

Entanglements are topological constraints of a polymer chain imposed by its neighbouring chains.

See slides 283 and 284 for a static model on the entanglement network.

See slides 288-290 for the tube model.

b) Show schematically the evolution of the stress as a function of $\log(t)$ during a relaxation test on a non-crosslinked amorphous polymer, indicating the rubbery plateau, the disentanglement time, τ_d, and the viscous regime. Interpret this behavior with the help of the tube model.

See slide 290.

c) According to Fick's law, the diffusion length is given by $(Dt)^{1/2}$, where D is the diffusion coefficient, which, in case of an entangled polymer chain diffusing inside the tube representing its interactions with its neighbors, will be proportional to M^{-1}. We can assume that the length of this tube, L, is also proportional to M. Show that τ_d varies as M^3 and that the self-diffusion coefficient of an entangled polymer (which describes the rate of diffusion of the center of mass of the chain) is proportional to M^{-2}.

As stated in the question, Fick's law tells us that the diffusion distance $x = \sqrt{Dt}$. The time that a chain needs to diffuse a distance $x = L$, and hence escape from its tube is:

$$\tau_d = \frac{L^2}{D} \propto \frac{M^2}{M^{-1}} = M^3$$

When the chain diffuses out of its tube after time τ_d, i.e., when one of its ends reaches the initial position of the other end, its centre of mass moves an average linear distance equal to its root-mean-square end-to-end distance, r_o, which is proportional to $\sqrt{M}$. Applying Fick's law to the centre-of-mass, we get

$$D_{\text{self-diffusion}} = \frac{r_o^2}{\tau_d} \propto \frac{\left(\sqrt{M}\right)^2}{M^3} = M^{-2}$$