Lesson 08: Ceramics and polymers

Exercise 08.1 Polychlorotrifluoroethylene

a) Sketch the repeat unit (C_2ClF_3)

$$\left[\begin{array}{ccccc} & Cl & & F & \\ & | & & | & \\ - & C & - & C & - \\ & | & & | & \\ & F & & F & \end{array}\right]$$

b) Calculate the molar mass of a monomer

(2*12+1*35.5+3*19) g/mol = 116.5 g/mol

c) Calculate the degree of polymerization in case of the molar mass of being 10^6 g/mol?

$$\bar{N} = \bar{M}/m = 1000000 \text{ g/mol}/116.5 \text{ g/mol} = 8580$$

d) What is the straightened chain length for a chain with molar mass 10^6 g/mol?

N is the number of bonds!

$$L = N_{CC} d_{CC} \sin(\theta_{CC}/2) = 2 * 8580 * 0.154 \text{ nm} * \sin(109°/2) = 2150 \text{ nm}$$

e) What is the start to end distance of a chain with a molar mass 10^6 g/mol?

$$r = d_{CC}\sqrt{N_{CC}} = 0.154 \text{ nm} * \sqrt{2 * 8580} = 20.2 \text{ nm}$$

Exercise 08.2: Ceramics

Magnesia is an ionic ceramic with the chemical formula MgO.

(a) Calculate the fraction of ionic bonding.

Electronegativities Mg 1.3 and O 3.5 leads to an ionic fraction *X* of 70%

(b) Predict the crystal structure of MgO based on the ionic radii of Mg^{2+} (72 pm) and O^{2-} (140 pm).

The ratio between the radii of 0.51 indicates halite structure (sodium chloride).

(c) Predict the density of MgO.

In the sodium chloride structure where both ions are sitting on their fcc sublattices. The lattice constant *a* is given by the sum of both diameters (a=2*72+2*140 pm = 424 pm). The cube of the unit cell contains 4 ions of each type; the molar mass of the unit cell hence becomes m = 4*(16+24.3) g/mol. The density

$$\rho = m/V = 4 \cdot 40.3 \text{ g/mol} / \left(6.022 \cdot 10^{23} \text{ mol}^{-1} \cdot \left(424 \cdot 10^{-10} cm\right)^3\right) = 3.51 \text{ g/cm}^3$$

(d) Compare with the density of pure Magnesium which is hexagonal and (almost) close packed. Why is MgO denser than the dense packed Mg, despite having lighter O atoms in the lattice?

The density of pure magnesium is only 1.7 g/cm^3 as the atomic radius 145 pm of Mg is twice the size of a magnesium ion!

Exercise 08.3 PE-C

Polyethylene can be modified by chlorination. This process leads to a substitution of hydrogen atoms by chlorine atoms.

a) Calculate the mass fraction (weight percentage) of chlorine in PE-C, if one fourth of the hydrogen atoms will be substituted by chlorine.

The chemical formula of polyethylene after replacing every fourth hydrogen by chlorine becomes C_2H_3Cl. The mass fraction consequently 1*35.5/(2*12+3*1+1*35.5) = 57 wt.% Cl

b) What changes in properties can be expected when PE is chlorinated to PE-C (e.g. mass density, melting temperature)?

Due to the heavier Cl atom, a higher mass density and a higher melting temperature is expected.

c) Is there a difference between PE-C and PVC? Explain your answer.
PE-C and PVC have both the same chemical composition, but the distribution of the chlorine atoms is different. The positions of the Cl atoms in PE-C are totally random, but strongly ordered in PVC. (Each monomer of PVC carries one Cl atom. Due to the polymerization process the Cl atoms are bond to every other carbon atom; they are actually all sitting on alternate sides of the chain, i.e. in a *syndiotactic configuration. Consequently, PVC has a stiffer chain*).

Exercise 08.4 Thermoplastic versus thermoset
Is it possible to cut polypropylene up for reusing the material?
Why are there efforts to replace thermosets by thermoplastics?

A thermoplastic can be re-heated and a new product can be shaped, but thermosets cannot be re-shaped. Polypropylene is thermoplastic and can be cut and reused.

Exercise 08.5 Biopolymers
Where can we find polymers in nature? Abundantly, cellulose, starch, DNA, proteins and many others. Chromosome 1 has 250 million base pairs (corresponding to degree of polymerization), with an average length of 0.34 nm per base pair, the length would be about 8.5 cm.

Exercise 08.6 Polymer Crystallinity
Two PET batches differ in mass density and crystallinity as follows

	Mass density	Crystallinity
Batch A	1.408 g/cm^3	74.3 %
Batch B	1.343 g/cm^3	31.2 %

What is the mass densities in completely crystalline and completely amorphous regions?

Crystallinity is the mass fraction of crystalline regions

$$x_{AB} = \frac{\rho_c}{\rho_{sc,AB}} \frac{\rho_{sc,AB} - \rho_a}{\rho_c - \rho_a}$$

From the two equations (one for each batch) the desired densities can be derived analytically (e.g. by hand or using Maple)

$$\rho_a = \frac{\rho_A \rho_B \left(x_A - x_B\right)}{x_A \rho_A - x_B \rho_B} = 1.2996 \text{ g/cm}^3$$

$$\rho_c = \frac{\rho_A \rho_B \left(x_A - x_B\right)}{\left(x_A - 1\right)\rho_A - \left(x_B - 1\right)\rho_B} = 1.4498 \text{ g/cm}^3$$