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

Polymer Science 2024

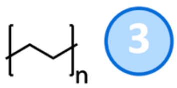
Exercise 2 – Solution

1. Classify the following polymers according to their rigidity (from 1 to 4, 1 for the most rigid and 4 for the least rigid): polyethylene, poly(ether ether ketone), poly(ethylene terephthalate), polypropylene. Explain your choice.

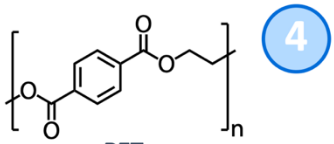
A few simple rules for rigidity (in the broadest sense of the term, because question 7 of Exercise 1 shows that it is not always directly correlated with structure):

benzene rings in the main chain = (much) more rigidity; side groups = more rigidity - they create barriers to rotation around single bonds, so the more bulky the side group, the higher will be the rigidity (here the CH_3 group of PP does not have a significant effect (see slide 78)).

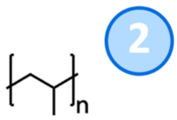
A surprisingly low C_∞ = 4.7 is assigned to PET, why it is indexed with the “4” below. This may, again, be because of definitions of catenary bonds that do not take individual bonds into consideration, or due to influence of flexible C-O single bonds.



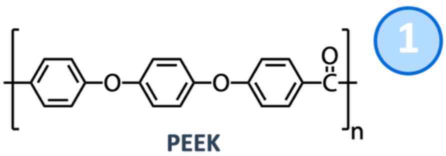
PE



PET



PP



PEEK

2. Place the following molecules into order of increasing boiling point: CH_4, CH_2O, CH_3OH. Explain your answer!

CH_4	**only London forces (lowest boiling point)**
CH_2O	**London forces and permanent dipole-dipole**
CH_3OH	**London forces, permanent dipole-dipole and hydrogen bonding (highest boiling point)**

3. Which of the following pairs has the highest melting point? Explain your answer!

a) pentane or octane? **–130 °C vs. –57 °C, London dispersion forces**

b) tetrahydrofuran (THF) or diethyl ether (Et_2O)? **–108 vs. –116 °C, permanent dipole only for THF.**

c) triethylamine or ethylamine? **–115 °C vs. –80 °C. Hydrogen bond formation only possible for ethylamine**

d) poly(ε-caprolactone) or nylon 6? **+ 60 °C vs. + 260 °C. Hydrogen bonding only possible for nylon 6.**

4. The origin of the polarity of molecules (like water) is in the electronegativity differences of the constituting atoms. Explain, why polyethylene is a non-polar polymer with no dipole moment, even though its constituting atoms (C and H) display electronegativity differences of 2.5 vs. 2.1. What about polyvinylchloride (PVC)?

Symmetrical molecules like methane have dipole moments that point from the four hydrogen atoms to the central carbon atom. The vector sum of the four vectors is zero and hence methane is a non-polar molecule. Water has two strong dipoles. The vector sum is not zero and it is therefore a polar molecule. Polyethylene is an example of a non-polar polymer. Each methylene unit has a weak dipole moment perpendicular to the chain axis. The net dipole moment for two adjacent methylene groups is, however, zero. Poly(vinyl chloride) is a polar polymer because of its strong C–Cl dipole moment and the lack of symmetry.

5. Which statement is wrong?

a) It is not possible to evaporate a polymer of large molar mass by simple heat input without chemically degrading it.

b) Cohesive energy is the energy required to separate molecules of a liquid/solid.

c) The compression modulus of a polymer depends little on temperature.

d) The intramolecular bonds of polymers are associated with energies on the order of 10 kJ/mol per repeating unit.

d)! Do not confuse intramolecular bonds with intermolecular bonds! ("intra" = "within".)

6. A hypothetical polymer chain of 100 segments of length a = 3 Å has the root-mean-square (RMS) end-to-end distance of 100 Å. Does this chain behave as an ideal freely-jointed chain? Calculate the number of Kuhn's statistical segments in the chain and the Kuhn's statistical segment length.

Don't use a calculator for this question. You will not be allowed to use one in the exam either.

The expected RMS end-to-end distance for an ideal freely jointed chain of this length is *an*^1/2 = 30 Å. The "real" RMS (= 100 Å) of this chain is greater than this number, therefore it does not behave as an ideal chain.

Flory's characteristic ratio:

$$C_\infty = \frac{\langle R_{\text{real}}^2 \rangle}{na^2} = \frac{100^2 \cdot \text{Å}^2}{100 \cdot 3^2 \cdot \text{Å}^2} \approx 11.1\ \text{Å}$$

The number of Kuhn segments:

$$N = \frac{na}{b} = \frac{na \cdot R_{\text{max}}}{na^2 \cdot C_\infty} = \frac{n}{C_\infty} = 9$$

The length of a Kuhn segment:

$$b = a \cdot C_\infty = 33.3\ \text{Å}$$

Reading suggestions:

- Lecture Notes of Chapters 2 and 3.1.

(You can download these documents from the Moodle-folder 'Reading Recommendation'.)