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

Polymer Science 2024

Exercise 1 – Solution

1. Conventionally, polymers are named according to a source-based or a structure-based convention, or using trade names (see reading recommendations). Draw the chemical structure (Lewis formulae) of the following polymers. Add the commonly used abbreviation and/or trade names where applicable.

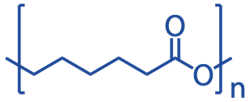
   poly(ethylene) → **Slide 17**;

   poly(vinyl alcohol), → **PE analogue, with one OH-group per repeating unit**;
   poly(tetrafluoroethylene) → **Slide 18**,

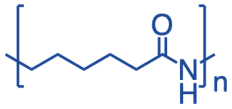
   poly(styrene) → **Slide 17**,

   poly(propylene) → **Slide 17**,

   poly(ε-caprolactone): **an aliphatic polyester**

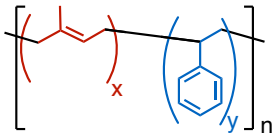


   nylon 6 **(corresponding polyamide, made from one single AB-type monomer)**

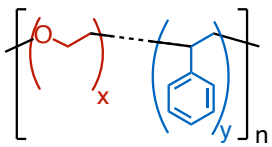


   poly(ethylene terephthalate) → **Slide 18**,

   poly(styrene-*b*-isoprene) → **block copolymer with solid line**,



   poly(styrene-*co*-(ethylene oxide)) → **random copolymer with dashed line**,



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poly(1-phenylethylene) → **this is polystyrene**!

2. A "model" of a linear poly(ethylene) chain with a molecular weight of 200'000 g/mol is constructed using a paper clip to represent one repeating unit. How many paper clips do you need? **200'000 / 28.05 = 7130**

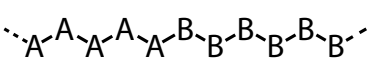
3. Calculate M_n and M_w for the following polymers:

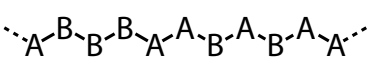
   a. A sample containing equal *masses* of polymers with molecular weights of 5,000 g/mol and 85,000 g/mol.

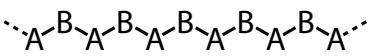
   b. A sample containing equal *moles* of polymers with molecular weights of 5,000 g/mol and 85,000 g/mol.

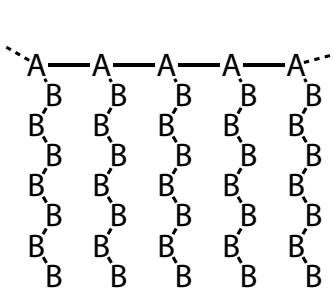
   a) Based on 17 x 5'000 g/mol and 1 x 85'000 g/mol:
   M_n = 9'444 g/mol; M_w = 45'000 g/mol
   b) Based on 1 x 5'000 g/mol and 1 x 85'000 g/mol:
   M_n = 45'000 g/mol; M_w = 80'556 g/mol

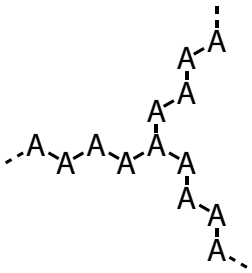
4. Name the following polymers based on their different architectures if A represents styrene monomers and B represents ethylene monomers. Use the reading recommendations.

a)


b)


c)


d)


e)


a) polystyrene-*block*-polyethylene;
b) poly(styrene-*ran*-ethylene);
c) poly(styrene-*alt*-ethylene);
d) polystyrene-*graft*-polyethylene;
e) 3-*star*-polystyrene

5. Why is M_w often preferred over M_n as a measure of molar mass? Consider the hypothetical case of a sample consisting of two chains of molar masses $M_1 >> M_2$. Discuss M_n and M_w in the limit of $M_2 \rightarrow 0$.

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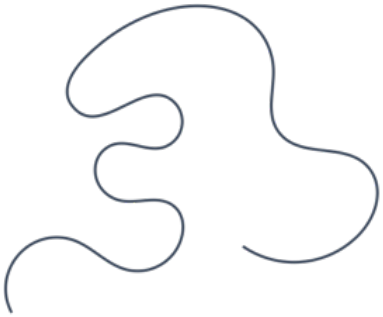
In short, because M_n is too much sensitive to low molar masses.

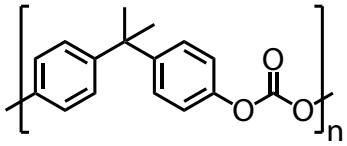


M_1 $\qquad$ $M_2 \to 0$

$$M_n = \frac{M_1}{2} \qquad M_w = M_1$$

6. What is the root of the mean of the square of the distance between the ends (R_n) of a chain of polyethylene with a molar mass of 140'000 g/mol? (C_∞ = 6.7, l = 0.15 nm)?
   Use the magic formula for $\langle R_n^2 \rangle$, which you hopefully already know by heart. The molar mass of a CH_2 group is 14 g/mol, n = 140,000/14 = 10,000, $R_n = (6.7 \times 10{,}000)^{1/2} \times 0.152$ nm = 38.83 nm

7. Below is the chemical formula for bisphenol A polycarbonate:



   Despite its apparently rigid structure (presence of benzene rings in the main chain), the polycarbonate has a C_∞ of 2.2 in methylene dichloride. This is because we consider the benzene group as only one catenary bond instead of 5. The average length of a bond becomes thus approximately (5 + 5 + 1 +1) / 4 = 3 times the length of a single C-C (or C-O) bond. What would the value of C_∞ be if we consider each link separately?

   Let's call the average length l. If the chain has n bonds according to the original definition, it will have 12 bonds if we consider each link separately. Since the value of $\langle R_n^2 \rangle$ must be independent of how we define a bond, we can state:

$$2.2 \cdot n_1 \cdot l_1^2 = C_\infty(new) \cdot n_2 \cdot l_2^2$$

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C_∞(new) is therefore equal to 4 x 2.2 x 9/12 = 6.6. (It is to note that C_∞ = 2.2 is not very realistic, but the point of the question is simply to show why C_∞ is so low for PC despite its seemingly rigid structure.)

8. Some properties of ideal polymers are independent of the chemical structure. For a simple treatment of all ideal polymers, one might define an equivalent freely jointed chain. This newly defined chain has the same mean-square end to-end distance, R_n, and the same maximum end-to-end distance R_{max} (projection length) as the actual polymer. Using this concept, a complex chemical structure simplifies to a straight chain of N Kuhn monomers with an effective length b (Kuhn length). Calculate the Kuhn length b of polypropylene. How many monomers make up one Kuhn monomer? Calculate the molecular weight M_0 of the Kuhn monomer.

   Hint: For the calculation of R_{max} use the all-*trans* conformation with a bond angle of θ = 68°.

$$b = \frac{< R_n^2 >}{R_{max}} = \frac{C_\infty \cdot n \cdot l^2}{R_{max}} \qquad R_{max} = nl\cos(\theta/2)$$

$$b = \frac{C_\infty \cdot n \cdot l^2}{nl\cos(\theta/2)} = \frac{C_\infty \cdot l}{\cos(\theta/2)} = \frac{6.8 \cdot 1.54\text{Å}}{\cos(34°)} = 12.6\text{Å}$$

$$N = \frac{C_\infty \cdot n \cdot l^2}{b^2} = \frac{R_{max}^2}{C_\infty \cdot n \cdot l^2} = \frac{n^2 l^2 \cos^2(\theta/2)}{C_\infty \cdot n \cdot l^2} = \frac{n\cos^2(\theta/2)}{C_\infty}$$

$$\frac{n}{N} = \frac{C_\infty}{\cos^2(34°)} \approx \frac{6.8}{0.6873} \approx 9.9 \longrightarrow \textbf{ca. 5 repeat units per Kuhn segment}$$

$$M_b = 5 \cdot 42.08\ g/mol \approx 210\ g/mol$$

9. An ideal polymer chain is often referred to as a Gaussian chain or Gaussian coil, because the Gaussian distribution successfully describes its end-to-end distance. Which assumptions are made in the Gaussian approximation? When does this approximation become valid? Can you imagine limitations of this approach?

   Tip: Use the reading recommendation.

   The Gaussian approximation is only valid for large n, and, as we will see later, will fail if the polymer chain segment length of interest becomes short. We will also note soon that the Gaussian distribution does not accurately describe the situation of large end-to-end distances (it even predicts a finite probability for end-to-end distances that are

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larger than the contour length, which is physically not plausible). Limitations that arise from that and workarounds will be discussed in Chapter 4.1.

Reading suggestions:

- P. Hodge *et al*., *Pure Appl. Chem*. **2020**, *92*, 797-813; **A concise guide to polymer nomenclature for authors of papers and reports in polymer science and technology (IUPAC Technical Report).**
- H. N. Cheng, B. A. Howell, *J. Chem. Edu.* **2017**, *94*, 1794-1797; **A Primer on Polymer Nomenclature: Structure-Based, Source-Based, and Trade Names**.
- T. Sakai, *Physics of Polymer Gels*. First Edition. Wiley-VCH Verlag GmbH & Co. KGaA (**2020**).

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

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