

**Polymer Science 2025/26**

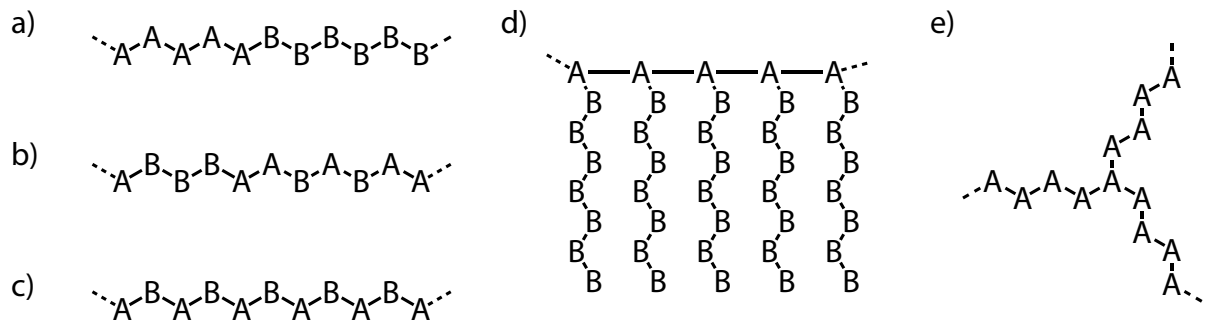
**Exercise 1**

1. Polymers can be named according to source-based conventions (derived from the monomer), structure-based conventions (IUPAC), or by common trade names (see reading recommendations). For each of the following polymers: draw the chemical structure (Lewis formula), provide the commonly used abbreviation, and add the trade names where applicable.

low-density polyethylene, poly(vinyl alcohol), poly(tetrafluoroethylene), polystyrene, polypropylene, poly( $\epsilon$ -caprolactone), polycarbonate, poly(vinyl chloride), nylon 6, poly(ethylene terephthalate), poly(styrene-*b*-isoprene), poly(ether ether ketone), poly(styrene-*co*-(ethylene oxide)), poly(1-phenylethylene).

Which of these polymers can be synthesized by free radical polymerization?

2. Styrene repeat units are represented as A and ethylene repeat units as B. Based on the schematic structures shown, name the corresponding polymers according to their architectures. Use the reading recommendations for guidance.



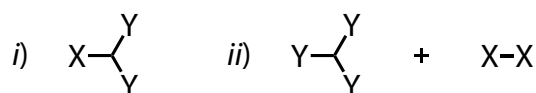
3. For the following polymer samples, calculate the number-average molar mass,  $M_n$ , and weight-average molar mass,  $M_w$  :
  - a. A sample containing equal *masses* of polymers with molar masses of 5'000 g/mol and 85'000 g/mol.
  - b. A sample containing equal *moles* of polymers with molar masses of 5'000 g/mol and 85'000 g/mol.

Why is  $M_w$  often considered a more representative measure of polymer molar mass than  $M_n$ ? Consider a hypothetical sample containing just two chains with molar masses  $M_1 \gg M_2$ . Discuss  $M_n$  and  $M_w$  in the limit of  $M_2 \rightarrow 0$ .

- Estimate the degree of polymerization for a linear polyethylene chain with a molar mass of 200'000 g/mol. Then, estimate its contour length, i.e. the length of the fully extended backbone, and compare it to its root-mean-square end-to-end distance.
- Sketch or indicate schematically three distinct solid-state structures that thermoplastic polymers can adopt at room temperature, depending on crystallinity and glass transition temperature. For each type, provide two example polymers.
- Explain the principle and main characteristics of a polycondensation and how it differs from polyaddition. Consider the polycondensation of
  - a mixture of X-X and Y-Y type monomers, where Y can react with X, and
  - a Y-X type monomer.

Both approaches can produce a linear polymer. What is the advantage of using a Y-X monomer? Why is the first approach usually preferred in practice?

Indicate the polymer architecture resulting from the polycondensation of the following systems? Tip: consider two growing macromolecules in each case.



- The radical polymerization of vinyl chloride can lead to different positional isomers. Explain why. Given that the free radical prefers to reside on the carbon adjacent to the chlorine atom (due to the electron-withdrawing effect of Cl) which chain form dominates? Draw a detailed reaction mechanism for the polymerization initiated by azobisisobutyronitrile (AIBN), including termination by disproportionation.
- In a polycondensation reaction, 20 g of hexamethylene diamine (1,6-diaminohexane) and 20 g of adipic acid (1,6-hexanedioic acid) are mixed. After 5 minutes, the remaining unreacted amine groups correspond to 30% of the initial amount ( $t = 0$ ). Calculate the current number-average degree of polymerization,  $\bar{X}_n$ . Determine the final  $\bar{X}_n$  at the end of the reaction. Identify the functional group(s) present at the chain ends.

Note: the limiting functional groups define the extent of the reaction (conversion).

**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.**

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