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

Polymer Science 2025/26

Exercise 1 – Solutions

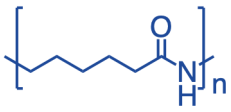
1. Polymers can be named according to source-based conventions (derived from the monomer), structure-based conventions (IUPAC), or by common trade names (see reading recommendations). For each of the following polymers: draw the chemical structure (Lewis formula), provide the commonly used abbreviation,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

   low-density polyethylene **(LDPE)**, poly(vinyl alcohol) **(PVA or PVOH)**, poly(tetrafluoroethylene) **(PTFE)**, polystyrene **(PS)**, polypropylene **(PP)**, poly(ε-caprolactone) **(PCL)**, polycarbonate **(PC)**, poly(vinyl chloride) **(PVC)**, nylon 6, poly(ethylene terephthalate) **(PET)**, poly(polystyrene-*b*-polyisoprene), poly(ether ether ketone) **(PEEK)**, poly(styrene-*co*-(ethylene oxide)), poly(1-phenylethylene) **(this is polystyrene!)**.

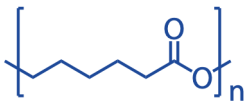
   Which of these polymers can be synthesized by free radical polymerization?

   For the chemical structures, see Slides 17, 18.

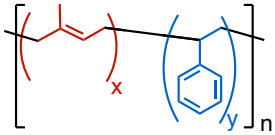
   nylon 6 (polyamide, made from one single AB-type monomer, see Slide 42)



   poly(ε-caprolactone): a corresponding aliphatic polyester



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



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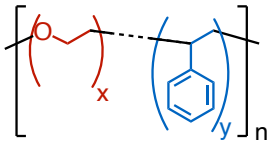
poly(styrene-*co*-(ethylene oxide)) → random copolymer with dashed line,



The polymers based on vinyl-type monomers (LDPE, PTFE, PS, PVC) can be polymerized by free radical polymerization.

Note: polypropylene (PP) is not polymerized by free radical polymerization (see Chapter 6). PVA is synthesized via the free-radical polymerization of poly(vinyl acetate), followed by hydrolysis of the acetate groups to hydroxyl groups.

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.

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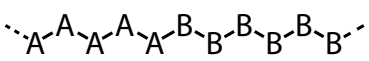

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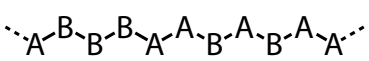

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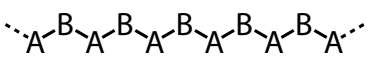

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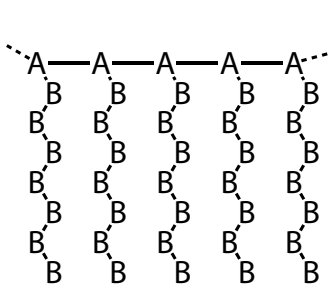

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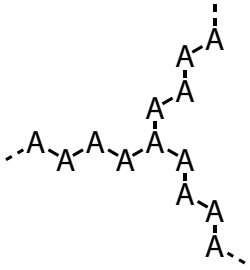

a) polystyrene-*block*-polyethylene;

b) poly(styrene-*ran*-ethylene);

c) poly(styrene-*alt*-ethylene);

d) polystyrene-*graft*-polyethylene;

e) 3-*star*-polystyrene

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.

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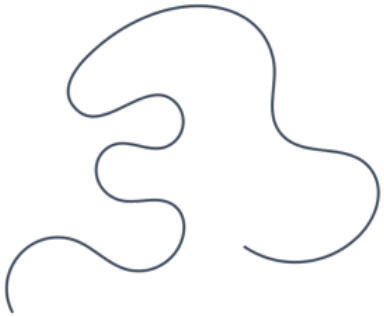
a. Based on 17 x 5'000 g/mol and 1 x 85'000 g/mol:
M_n = 9'444 g/mol; M_w = 45'000 g/mol

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

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 >> M_2. Discuss M_n and M_w in the limit of $M_2 \rightarrow 0$.

In short, because M_n is too much sensitive to low molar masses. The physical properties will certainly be determined by the long polymer, which is better reflected by M_w.



M_1 $\qquad$ $M_2 \rightarrow 0$

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

4. 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.

$$X_n = \frac{200'000\ \text{g/mol}}{28.05\ \text{g/mol}} = 7130$$

A repeating unit has two C-C bonds of length a = 1.54 Å:

$$l = 7130 \cdot 2 \cdot 1.54\ \text{Å} \approx 21940\ \text{Å} \equiv 2.2\ \mu\text{m}$$

$$R_g = \sqrt{C_\infty n a} = \sqrt{6.7 \cdot 2 \cdot 7130} \cdot 1.54\ \text{Å} \approx 48\ \text{nm}$$

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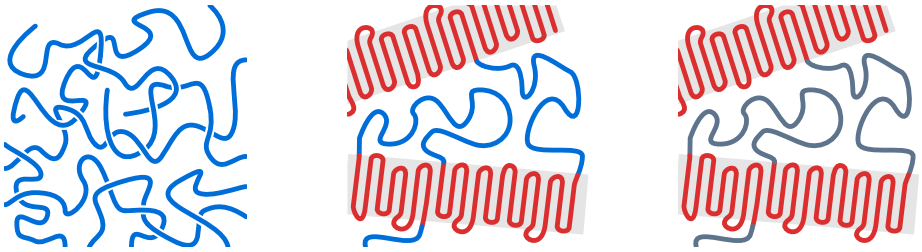


glassy	semicrystalline, glassy	semicrystalline
T_g > r.t.	T_m > T_g > r.t.	T_m > r.t., T_g < r.t.
PS ($T_g \approx 100$ °C)	PET ($T_m \approx 250$ °C, $T_g \approx 60$ °C)	LDPE ($T_m \approx 110$ °C, $T_g \approx -100$ °C)
PC ($T_g \approx 150$ °C)	Nylon 6 ($T_m \approx 220$ °C, $T_g \approx 50$ °C)	PP ($T_m \approx 170$ °C, $T_g \approx -10$ °C)

5. 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.

6. Explain the principle and main characteristics of a polycondensation and how it differs from polyaddition. Consider the polycondensation of

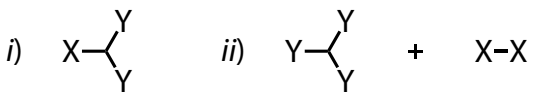
   - a mixture of X-X and Y-Y type monomers, where Y can react with X, and
   - a Y-X type monomer.

   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?

   See Slides 41–47 and Reader.

   Y-X type monomers have the advantage of a built-in stoichiometric balance between functional groups (see the general Carothers equation). In practice, however, symmetric X-X and Y-Y monomers are usually preferred, because Y-X monomers are potentially unstable during storage: their two complementary groups can react with each other prematurely. By contrast, X-X and Y-Y monomers can be stored separately, which prevents undesired self-reaction before polymerization.

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



   In the first case, a "hyperbranched" polymer is obtained. Initially, the Y groups of the monomer react with X groups of other monomers, leaving only Y groups

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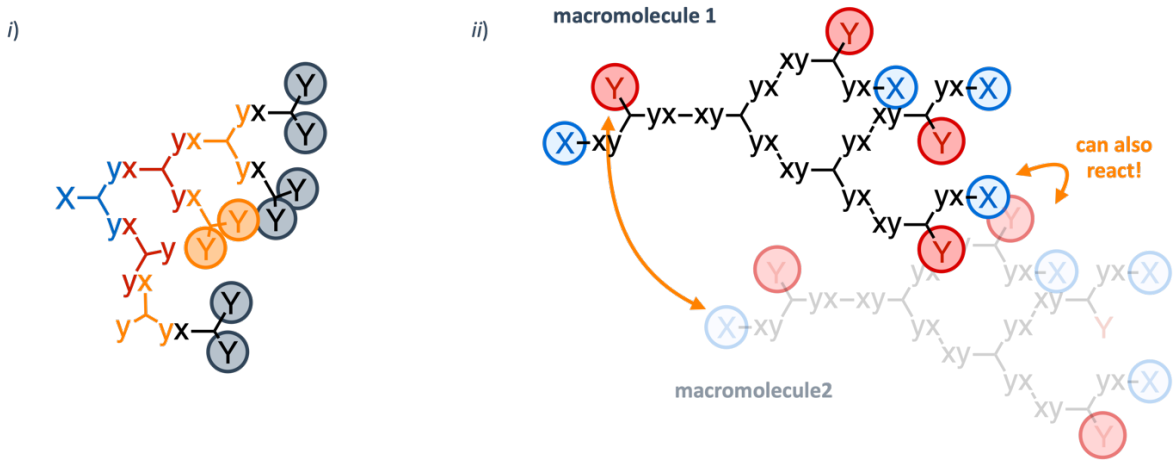
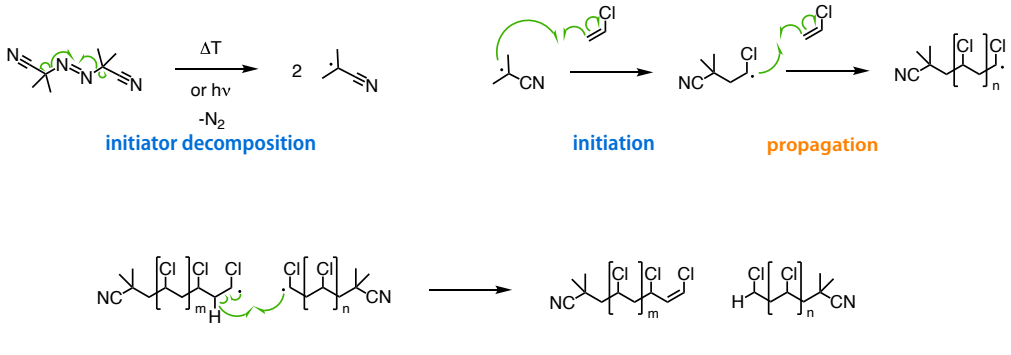
exposed on the surface of the growing macromolecule (highlighted in the circles below). The initial X group of the first monomer is rapidly consumed though ring formation and can be ignored. Since Y groups cannot react with each other, each macromolecule continues to grow only by adding new monomers, without reacting with neighboring macromolecules. The result is an independent, hyperbranched architecture without intermolecular crosslinking.

In the second case, when a Y group reacts with an X-X monomer, it generates a new X group. This X group can then react with a trifunctional Y-based monomer, leaving a Y group exposed. As a result, the growing macromolecule quickly shows both X and Y groups on its surface. These do not only react with the monomers present, but also with the complementary groups of neighboring macromolecules, which rapidly leads to the formation of a densely crosslinked polymer network.



7. 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.



See Slide 62 for the predominant head-to-tail arrangement (sequence isomerism).

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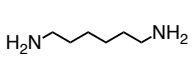
8. In a polycondensation reaction, 20 g of hexamethylene diamine (1,6-diaminohexane) and 20 g of adipic acid (1,6-hexanedioic acid) are mixed. After 5 minutes, the remaining unreacted amine groups correspond to 30% of the initial amount (t = 0). Calculate the current number-average degree of polymerization, $\bar{X}_n$. Determine the final $\bar{X}_n$ at the end of the reaction. Identify the functional group(s) present at the chain ends.

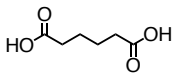
   Note: the limiting functional groups define the extent of the reaction (conversion).



1,6-diaminohexane

$C_6H_{16}N_2$
molar mass: 116.2 g/mol

20 g (0.172 mol)



adipic acid

$C_6H_{10}O_4$
molar mass: 146.1 g/mol

20 g (0.137 mol)

stoichiometric imbalance: $r = 0.8$

consumed at t = 5 min: $0.172\ \text{mol} - 0.3 \cdot 0.172\ \text{mol} = 0.120\ \text{mol}$

conversion of COOH groups: $p = \frac{0.120\ \text{mol}}{0.137\ \text{mol}} = 0.88$

current $\bar{X}_n$: $\bar{X}_n(t = 5\ \text{min}) = \frac{1+r}{1+r-2pr} = 4.6$

final $\bar{X}_n$: $\bar{X}_n(t = \infty) = \frac{1+r}{1+r-2pr} = 9$

Since all COOH groups are consumed, the chain will have amino end groups. Note that only oligomers are obtained at the given stoichiometric imbalance, regardless of the 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'.)

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