Organic Chemistry – Exercise 9

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Help: December 18, 2025

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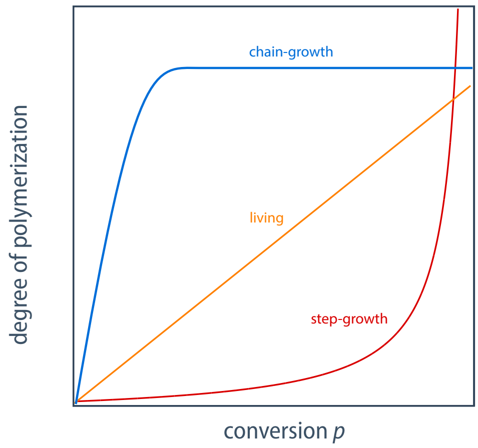
1. There are many different ways in which polymers can be synthesized. Different techniques used for polymer synthesis occur through different mechanisms, follow different kinetics and yield products with different properties.

   a. Qualitatively sketch the degree of polymerization evolution with conversion for step-growth, chain-growth and living polymerizations.



   b. What are the conditions that are usually required for obtaining polyesters with high molar mass in polycondensation reactions? How can you achieve them experimentally?

   Exact 1:1 ratio of functional groups, and the reaction should be carried out up to high conversions (Carothers equation). To achieve the latter, polycondensation reactions should be carried out at high temperature and/or reduced pressure, in an open system, to ensure the removal of the small molecule side product from the system. The reactants should be used in stoichiometric balance.

   c. What are the three possible ways in which the growth of a polymer chain can end in the case of free cationic polymerizations?

   The growing polymer chains can be terminated by combination with counterions potentially present in the system or by quenching with nucleophiles, or it can undergo chain transfer to monomer (which terminates a single chain but starts a new one).

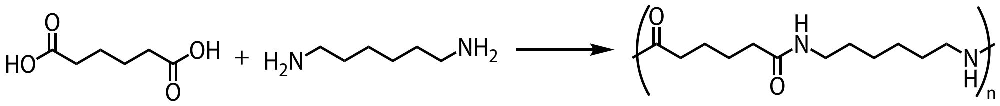
   d. Which polymerization pathway is the most reliable for the synthesis of block copolymers of desired molar mass and composition?

   In order to obtain block copolymers with desired properties in a controlled manner, it must be ensured that all chain ends are active before introducing the new monomers in the system, and that is the case only in living chain polymerization, of which the students only know free anionic

polymerization. All the other polymerization pathways have some degree of termination or transfer.

2. Polycondensation of an equimolar mixture of adipic acid (1,6-hexanedioic acid) and hexamethylenediamine (hexan-1,6-diamine) is carried out at 200 °C until the conversion of 99 % is reached.

   a. Show the chemical reaction that describes the synthesis of this polymer. What polymer family does the product belong to?



   The resulting polymer is a polyamide.

   b. Calculate the number-average molar mass and the weight-average molar mass of the obtained polymer.

   According to the task, the amine and carboxyl groups are present in equal amounts (r = 1). When that is included in the Carothers equation we observe:

$$\overline{X_n}=\frac{1+r}{1+r\text{-}2rp}=\frac{1+1}{1+1-2\cdot 1\cdot 0.99}=100.$$

   The number-average molar mass can be calculated by multiplying the number-average degree of polymerization with the molar mass of the repeat unit:

$$M_n=M_o\cdot\overline{X_n}=226\,\frac{\text{g}}{\text{mol}}\cdot 100=22.6\,\frac{\text{kg}}{\text{mol}}.$$

   The weight-average molar mass can be calculated in two alternative ways. One is by using the weight-average degree of polymerization:

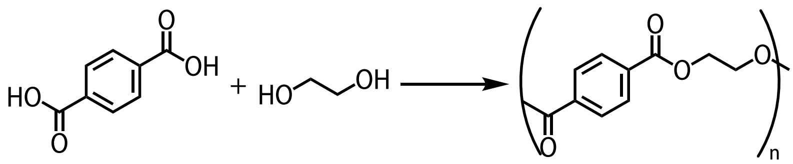
$$M_w=M_o\cdot\overline{X_w}=M_o\cdot\frac{1+p}{1-p}=226\,\frac{\text{g}}{\text{mol}}\cdot\frac{1+0.99}{1-0.99}=45.0\,\frac{\text{kg}}{\text{mol}}.$$

   The other way is by using the dispersity:

$$M_w=Đ\cdot M_n=(1+p)\cdot M_n=(1+0.99)\cdot 22600\,\frac{\text{g}}{\text{mol}}=45.0\,\frac{\text{kg}}{\text{mol}}.$$

3. Poly(ethylene terephthalate) is a polyester that is most frequently used in the production of plastic bottles for carbonated drinks due to its high barrier properties for CO_2. This polymer can be synthesized via polycondensation reaction from terephthalic acid (TA) and ethylene glycol (EG) (ethan-1,2-diol). Consider that the reaction was carried out until the conversion reached 99 %.

   a. Show the chemical reaction that describes the synthesis of this polymer. What polymer family does the product belong to?



   The resulting polymer is a polyester.

b. If there was 1 mol% excess of EG in the system, calculate the number-average molar mass of the obtained polymer.

As EG is present in 1 mol% excess (r = 1/1.01 = 0.99), from the Carothers equation we calculate the number-average degree of polymerization:

$$\overline{X_n}=\frac{1+r}{1+r\text{-}2rp}=\frac{1+0.99}{1+0.99-2\cdot0.99\cdot0.99}=66.8.$$

The number-average molar mass can be calculated by multiplying the number-average degree of polymerization with the molar mass of the repeat unit:

$$M_n=M_o\cdot\overline{X_n}=192\,\frac{\mathrm{g}}{\mathrm{mol}}\cdot66.8=12.8\,\frac{\mathrm{kg}}{\mathrm{mol}}.$$

c. If there was 2 mol% excess of EG in the system, calculate the number-average molar mass of the obtained polymer.

Similarly to the previous task (r = 1/1.02 = 0.98):

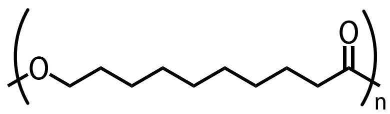
$$M_n=M_o\cdot\overline{X_n}=M_o\cdot\frac{1+r}{1+r\text{-}2rp}=192\,\frac{\mathrm{g}}{\mathrm{mol}}\cdot\frac{1+0.98}{1+0.98-2\cdot0.98\cdot0.99}=9.6\,\frac{\mathrm{kg}}{\mathrm{mol}}.$$

d. Comment on the difference between the values obtained in b) and c).

By changing the stoichiometric ratio by only 1 % the resulting molar mass decreases by ~25 %. This emphasizes the importance of the effect of the ratio of functional groups on the molar mass of the resulting polymer.

4. Monomers that contain both hydroxyl and carboxylic groups are usually attractive for polycondensation reactions.

a. Draw the structure of the polymer obtained by polymerizing pure ω-hydroxydecanoic acid (HO-$(CH_2)_9$COOH).



b. Calculate the mass of lauryl alcohol (1-dodecanol) which should be added to 470 g of ω-hydroxydecanoic acid in order to obtain a polyester with the number-average molar mass of 4000 g/mol under the conditions where full conversion is ensured.

The molar mass of the repeating unit is M_0=170 g/mol, so the number-average degree of polymerization is $\overline{X_n}=M_n/M_0$=23.53. As the full conversion is assumed, using the Carothers equation we can calculate the ratio of functional groups:

$$\overline{X_n}=\frac{1+r}{1+r\text{-}2rp}\ \text{->}\ r=\frac{\overline{X_n}-1}{\overline{X_n}+1}=0.918.$$

As hydroxyl and carboxylic groups are present in equal amount in ω-hydroxydecanoic acid (ωHDA), the hydroxyl groups of lauryl alcohol (LA) will create an excess of hydroxyl groups:

$$r=\frac{n_{COOH}}{n_{OH}}=\frac{n(\omega\mathrm{HDA})}{n(\omega\mathrm{HDA})+n(\mathrm{LA})}\ \text{->}\ n(\mathrm{LA})=n(\omega\mathrm{HDA})(1/r\text{-}1)=0.223\ \mathrm{mol}.$$

The required mass of lauryl alcohol is m(LA) = n(LA)*M(LA) = 0.223 mol*186 g/mol = 41.5 g.