

Organic Chemistry – Exercise 10

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1. A polymerization of styrene (vinylbenzene) is carried out at 60 °C with dibenzoyl-peroxide as the initiator. The initial concentration of styrene is 8.74 mol/L, and the initial concentration of dibenzoyl-peroxide is 0.02 mol/L. Transfer to monomer can be neglected in this case. Moreover:

$$f = 0.64$$

$$k_d = 3.00 \cdot 10^{-6} \text{ s}^{-1}$$

$$k_p = 176 \text{ L mol}^{-1} \text{ s}^{-1}$$

$$k_t = 3.60 \cdot 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$$

- a. Show the chemical mechanism of the initiator decomposition, initiation, and the propagation reaction.

- b. Show the mechanism of the termination by combination.

2. A polymerization of methyl methacrylate (MMA) is carried out with azobis(isobutyronitrile) (AIBN) as the initiator in a way that the rate of initiation is $1.00 \cdot 10^{-8} \text{ L mol}^{-1} \text{ s}^{-1}$. This reaction is done "in bulk", meaning that there is no solvent in the system, but the liquid monomer has the function of the solvent. In that case, the mass concentration of the monomer can be estimated to be equal to its density. All transfer reactions can be neglected. Moreover:

$$\rho(\text{MMA}) = 0.944 \text{ g cm}^{-3}$$

$$fk_d = 1.00 \cdot 10^{-7} \text{ s}^{-1}$$

$$k_p = 143 \text{ L mol}^{-1} \text{ s}^{-1}$$

$$k_t = 6.10 \cdot 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$$

- a. Show the mechanism of the initiation, propagation and termination by disproportionation.

- b. Calculate the required concentration of AIBN in this system.

- c. Calculate the concentration of the active macroradicals in this system.

- d. Calculate the degree of polymerization and the number-average molar mass of the polymer obtained in this reaction.
- e. How would the degree of polymerization differ if 10 times more AIBN is present in the system? Support your answer with calculations.
3. Styrene is a monomer that can be polymerized via different polymerization methods.
- a. Considering its structure, explain why styrene can be polymerized via radical, free cationic and free anionic polymerizations.

Trifluoromethylsulfonic acid ($\text{F}_3\text{CSO}_3\text{H}$) can be used as an initiator when the following monomers are polymerized via free cationic polymerization: *i*) styrene; *ii*) (prop-1-en-2-yl)benzene and *iii*) p-methoxy(prop-1-en-2-yl)benzene. The observed initiation rates are $k_1 = 10^3 \text{ M}^{-1} \text{ s}^{-1}$; $k_2 = 5 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $k_3 = 10 \text{ M}^{-1} \text{ s}^{-1}$ (not in order).

- b. Draw the structures of the three monomers mentioned above.

c. Show the reaction describing the initiation reaction when styrene is used as a monomer.

d. Match the given monomers with their corresponding initiation rates. Explain your answer by comparing the relative stability of the formed cations.