

## Organic Chemistry – Exercise 10

Distribution: December 11, 2025

Help: December 18, 2025

Return until: December 21, 2025

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:

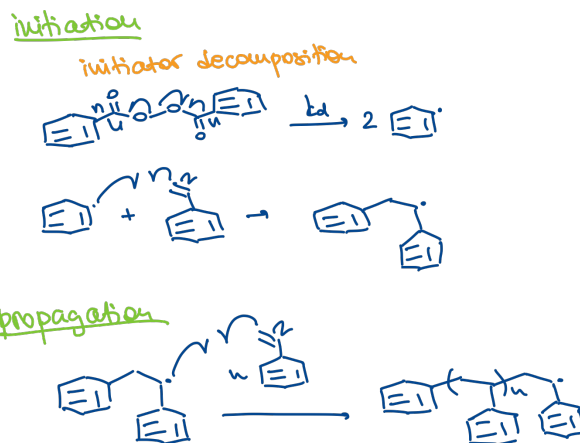
$$f = 0.64$$

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

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

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

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



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



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

**The rates of initiation and termination have to be the same:**

$$r_i = r_t \rightarrow 2fk_d[I] = 2k_t[M\cdot]^2 \rightarrow [M\cdot] = \sqrt{\frac{fk_d[I]}{k_t}} = 3.27 \cdot 10^{-8} \text{ M.}$$

- d. Calculate the initial rate of propagation.

$$r_p = k_p \sqrt{\frac{fk_d}{k_t}} [I][M] = 5.02 \cdot 10^{-5} \text{ M/s.}$$

- e. Calculate the degree of polymerization! What would be the degree of polymerization if termination occurred via disproportionation instead of combination?

**As the termination is occurring via combination,  $\bar{X}_n = 2\bar{v}$ :**

$$\bar{X}_n = \frac{k_p[M]}{\sqrt{fk_d k_t[I]}} = 1308.$$

**If the termination is occurring via disproportionation,  $\bar{X}_n = \bar{v}$ :**

$$\bar{X}_n = \frac{k_p[M]}{2\sqrt{fk_d k_t[I]}} = 654.$$

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:

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

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

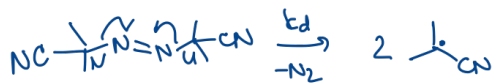
$$k_p = 143 \text{ L mol}^{-1} \text{ s}^{-1}$$

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

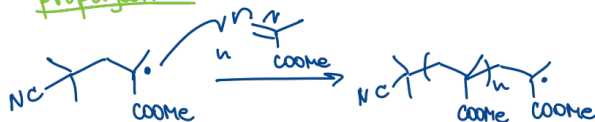
- a. Show the mechanism of the initiation, propagation and termination by disproportionation.

initiation

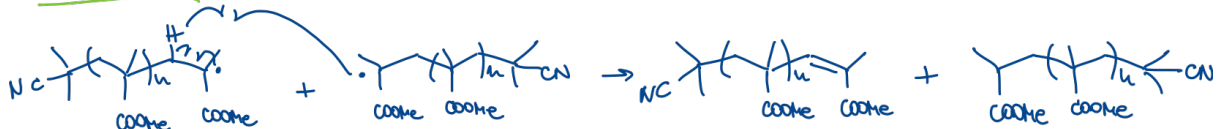
initiator decomposition



propagation



termination



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

**From the rate of initiation we get:**

$$r_i = 2fk_d[I] \rightarrow [I] = \frac{r_i}{2fk_d} = 0.05 \text{ M.}$$

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

Similarly as in the previous exercise:

$$[M \cdot] = \sqrt{\frac{fk_d[I]}{k_t}} = 2.86 \cdot 10^{-8} \text{ M.}$$

- d. Calculate the degree of polymerization and the number-average molar mass of the polymer obtained in this reaction.

As the termination is occurring via disproportionation,  $\bar{X}_n = \bar{\nu}$ :

$$\bar{X}_n = \frac{k_p[M]}{2\sqrt{fk_dk_t[I]}} = 3865 \rightarrow M_n = M_0 \cdot \bar{X}_n = 386.5 \text{ kg/mol.}$$

- e. How would the degree of polymerization differ if 10 times more AIBN is present in the system? Support your answer with calculations.

$$\bar{X}_n = \frac{k_p[M]}{2\sqrt{fk_dk_t[I]}} = 1222.$$

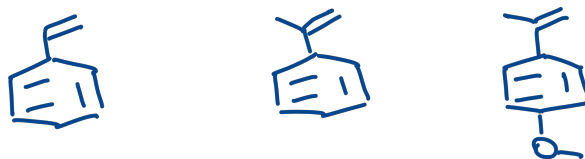
The degree of polymerization decreases with the increase of initiator concentration.

3. Styrene is a monomer that can be polymerized via different polymerization methods.
- Considering its structure, explain why styrene can be polymerized via radical, free cationic and free anionic polymerizations.

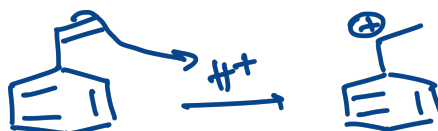
When styrene is polymerized via all the mentioned mechanistic pathways, the reactive center (radical, carbocation, carbanion) is on the benzyl C carbon (carbon atom directly connected to a benzene ring). The corresponding *p* orbital is aligned with the  $\pi$ -system of the benzene ring, so the system is stabilized by resonance, and the benzene ring can serve both as a +M or a -M substituent.

Trifluoromethylsulfonic acid ( $F_3CSO_3H$ ) 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).

- Draw the structures of the three monomers mentioned above.



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



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

All of the obtained cations are benzyl cations, which are stabilized by resonance. As the cation from compound *ii*) is tertiary and the one from compound *i*) is secondary, it is expected that the tertiary one would be more

stable. In compound *iii*) there is a methoxy group in *para* position, which is electron donating group that can further stabilize the formed cation. The more stable the formed cation, the faster the initiation process. So  $k_1$  corresponds to compound *ii*),  $k_2$  corresponds to compound *iii*) and  $k_3$  corresponds to compound *i*).