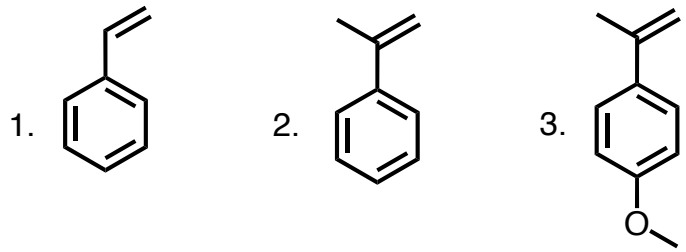
Organic Chemistry – Exercise 10

Distribution: December 13, 2024
Help: December 19 2024
Return until: January 15, 2025

1.

a. Qualitatively sketch the molar mass distributions for both step-growth and chain-growth polymerization at low, medium, and high conversion and explain the major differences.
b. Give the Schulz Flory weight distribution function (that is the same for both cases). How can it be the same if the evolution with conversion is different (as discussed in a.)

2. You measured the following rate constants of initiation by trifluoromethanesulfonic acid (CF_3SO_3H) of three vinylic monomers: 1. k_1: 10 L mol^{-1} s^{-1}; 2. k_2: 10^3 L mol^{-1} s^{-1}; 3. k_3: $5 \cdot 10^4$ L mol^{-1} s^{-1}.



a. Formulate the initiation and propagation mechanism of the polymerization of styrene (monomer 1).
b. Qualitatively explain the differences in the observed values of k.
c. In the case of the polymerization of styrene, there exists a secondary reaction involving the elimination of a β-hydrogen. Draw the reaction scheme of the net reaction and explain if it is a transfer or an elimination reaction.

3. Consider the free-radical polymerization of methyl methacrylate (MMA) initiated by azobis(isobutyronitrile) (AIBN) under the following reaction conditions:

$$[\text{AIBN}] = 10^{-2}\ \text{mol L}^{-1} \text{ and } [\text{MMA}] = 10\ \text{mol L}^{-1}$$

$$f = 0.6$$

$$k_\text{d} = 8.5 \cdot 10^{-6}\ \text{s}^{-1}$$

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

$$k_\text{t} = 7.2 \cdot 10^{7}\ \text{L mol}^{-1}\ \text{s}^{-1}$$

   a. Determine the propagation rate of polymerization.
   b. Determine the degree of polymerization assuming no chain transfer reaction to occur and that termination reactions occur exclusively by combination.
   c. The same polymerization is then performed with dicumyl peroxide (DCPO) as the initiator with the same concentration. The decomposition reaction of DCPO is three times as fast as compared to AIBN and we assume the efficiency factor *f* to be the same. What is the resulting effect the polymerization rate and the kinetic chain length?

4.

   a. What are the criteria necessary for a polymerization to be considered "living"?
   b. Why is living polymerization the only reliable pathway for obtaining block copolymers of precise composition and molar masses?