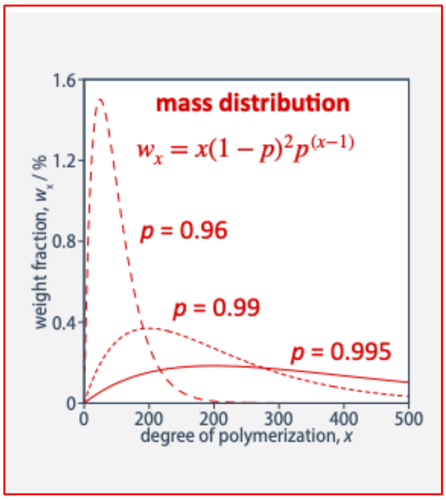
Organic Chemistry – Exercise 10 Mastersheet

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

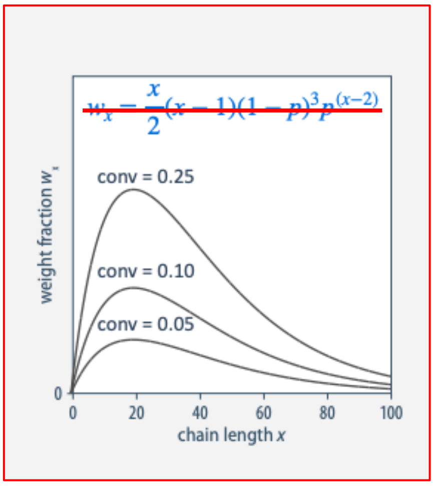
1.

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.

Step growth:



Chain growth:



There is an error in the slides, the equation in the weight distribution graph of chain growth polymerization is false. The correct equation is the same than in step-growth.

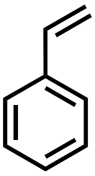
In step-growth polymerization, high molar mass polymers can only be obtained with very high conversion, while in chain growth polymerization, high molar mass polymers are already obtained at low conversions.

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.)?

$$\boxed{w_x = \frac{m_x}{\sum m_x} = \frac{N_x(x\bar{M}_0)}{N_0\bar{M}_0} = \frac{xN_x}{N_0} = x(1-p)^2p^{x-1} \ .}$$

p has different definitions in the two cases. In chain-growth, p is defined as a relative probability of a propagation step (the probability that a monomer addition will occur), i.e., as the rate of propagation divided by the sum of rates of all reactions that a propagating radical may undergo. In step-growth polymerization, in a system initially containing N0 difunctional monomers whose two functional groups can react with one another (assuming that ring formation is negligible), the probability that one such coupling reaction has occurred is then equivalent to the conversion p.

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}.

1.


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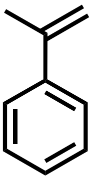

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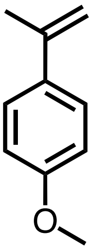
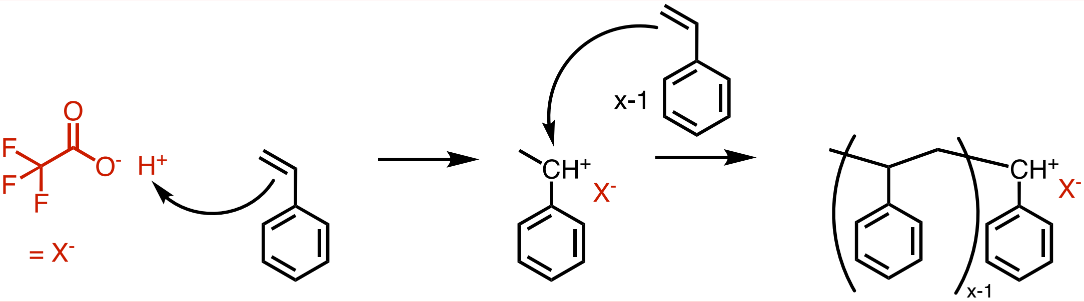


   a. Formulate the initiation and propagation mechanism of the polymerization of styrene (monomer 1).

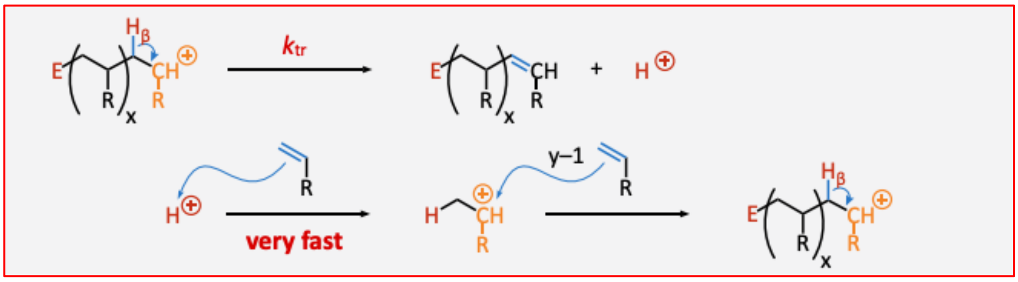


   b. Qualitatively explain the differences in the observed values of k.

The more stable the carbocation is, the faster the initiation. In styrene, the bezene exerts a +M effect stabilizing the positive charge. But there is an additional +I effect of the methyl group in monomer 2 and an additional +M effect provided by the ether in monomer 3.

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.

Chain transfer reaction to the monomer.



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

Note: Two notations were used in the slides, k_d and k_i. It made it confusing. We have changed everything to k_i (here and in the slides).

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

$f = 0.6$

$k_\mathrm{i} = 8.5 \cdot 10^{-6}\ \mathrm{s^{-1}}$

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

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

a. Determine the propagation rate of polymerization.

$$R_p = k_p \sqrt{\frac{f k_i [\mathrm{I}]}{k_t}}\,[\mathrm{M}]$$

R_p = 4.68*10^{-5} mol/L/s

b. Determine the degree of polymerization assuming no chain transfer reaction to occur and that termination reactions occur exclusively by combination.

$$\bar{\nu} = \frac{R_p}{R_i} = \frac{k_p[\mathrm{M}]}{2(fk_i k_t[\mathrm{I}])^{1/2}} \qquad X_n = 2\bar{\nu}$$

X_n = 2*459 = 918

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?

$$R_p = k_p\sqrt{\frac{fk_i[\mathrm{I}]}{k_t}}[\mathrm{M}]$$

polymerization rate will be increased by √3

$$\bar{\nu} = \frac{\mathrm{k_p[M]}}{2\sqrt{\mathrm{k_t f k_i [I]}}}$$

kinetic chain length will be reduced by **1/√3**

4.

a. What are the criteria necessary for a polymerization to be considered “living”?

Linear increase of molar mass with conversion

Number average molar mass depends on monomer/initiator ratio

Chain ends remain active after full monomer consumption (no termination or transfer)

b. Why is living polymerization the only reliable pathway for obtaining block copolymers of precise composition and molar masses?

The procedure to synthesize block copolymer is as follows: initiator is added to a solution of monomer A. After full consumption of monomer A, monomer B is added to the solution.

Therefore, to obtain block copolymers in a controlled manner we must make sure that all chain ends are still active before the addition of monomer B, and that is only possible in living polymerization