MSE 214 (Polymers)
Exercise 3 — Synthesis (II)
1st October 2025

Question 1.

Describe the three phases of radical chain-growth polymerization. Please include the relevant equations in your description. E.g. A + B → AB

Hint: Use I to denote the initiator species and M to denote the monomeric species.

Question 2.

List three differences between step-growth and chain-growth polymerization.

Question 3.

For a system of monomers that can undergo chain-growth polymerization, how do we dictate which stimuli (heat, light, etc.) is used to synthesize the polymer?

Assume that the identity of the radical does not impact the polymerization process.

Question 4.

For a radical polymerization with bimolecular termination, the polymer produced contains 1.30 initiator fragments per polymer molecule. Calculate the relative extents of termination by disproportionation and coupling, assuming that no chain-transfer reactions occur.

Question 5.

In the lecture, we discussed how chain "back-biting" causes the formation of short branches (Figure 1).

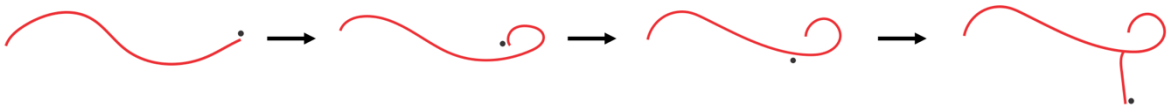
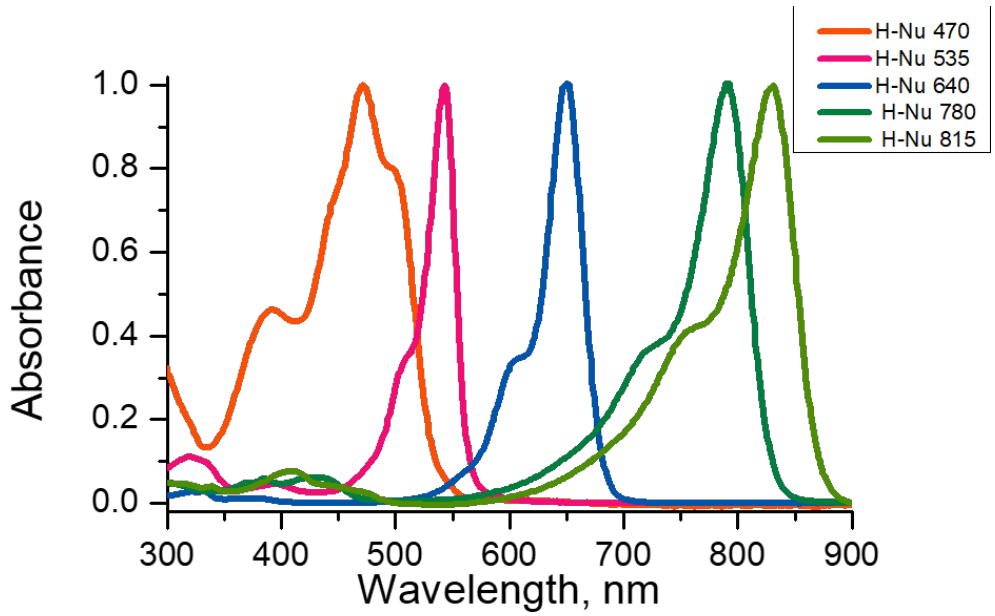


Figure 1. Schematic of "back-biting" that leads to the formation of short branches.

Using what you know about chain transfer, draw a schematic that describes the formation of long branches.

Question 6.

You are looking to run a chain-growth photopolymerization reaction using light of wavelength between 750 – 800 nm. The supplier you are working with gives you the plot below of absorbance vs. wavelength for some of their photoinitiators. Using this information, which photoinitiator(s) would work for your reaction? Explain why you think so. Assume that the quantum efficiency of all the photoinitiators are similar.



Question 7.

Rate constants for termination k_t are on the order of 10^8 L/mol.s in most free radical polymerizations. Consider the polymerization of styrene initiated by AIBN at 60˚C. For a solution of 0.01 M AIBN and 1.0 M styrene in benzene, the rate of polymerization (R_p) is 1.5 x 10^{-7} mol/L.s and M_n of the polymer produced is 138'000 g/mol. The repeat unit molecular weight is 104 g/mol and termination can be assumed to go 100% by coupling. Assume that the initiator efficiency of AIBN is 1. AIBN is the initiator here.

Using the information above, estimate the rate constant for propagation, k_p, for styrene at 60˚C.

Hint 1: What is the relationship between X_n and R_p and R_i?
Hint 2: Find the rate constant of dissociation k_d
Hint 3: Which equations feature both k_d and k_p?
Hint 4: The units of k_p is L/mol.s