1. Hexamethylene diamine ($H_2N\text{-}(CH_2)_6\text{-}NH_2$) is reacted with sebacoyl chloride ($Cl\text{-}OC\text{-}(CH_2)_8\text{-}COCl$) to form a polyamide (Nylon 6,10).

a) Write out the reaction of these two monomers, indicating the structure of the polymer formed and any byproducts of the reaction.

$$n\ H_2N-(CH_2)_6-NH_2 + n\ Cl-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow$$

$$H\left[\underset{H}{\underset{|}{N}}-(CH_2)_6-\underset{H}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}-(CH_2)_8-\underset{O}{\underset{\|}{C}}\right]_n Cl + (2n-1)\,HCl$$

b) Is this a step growth (condensation) polymerization or a chain growth (addition) polymerization?

step growth

c) Two separate polymerizations of these reactants are carried out, producing batches A and B. These are mixed (without further reaction) in amounts indicated in the table below. Calculate the number average molecular weight M_n of the mixture and the weight average molecular weight M_w of the mixture. Show you work, and put your final answers in the table.

Batch	Weight (g)	M_n (g/mole)	M_w (g/mole)
A	50	24,000	47,710
B	15	185,000	370,000
mixture	65	30,030	122,080

	$wt = \Sigma n_i M_i$	$M_n = \frac{\Sigma n_i M_i}{\Sigma n_i}$	$M_w = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i}$	$\Sigma n_i = \frac{wt}{M_n}$	$\Sigma n_i M_i^2 = wt \cdot M_w$
A	50	24,000	47,710	2.083×10^{-3}	2.386×10^{6}
B	15	185,000	370,000	8.108×10^{-5}	5.550×10^{6}
Mix	65			2.164×10^{-3}	7.936×10^{6}

$$M_{n,mix} = \frac{\Sigma n_i M_i}{\Sigma n_i} = \frac{65\ g}{2.164 \times 10^{-3}} = 30,030\ g/mole$$

$$M_{w,mix} = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i} = \frac{7.936 \times 10^{6}}{65} = 122,080\ g/mole$$

d) For the polymerizations above, assuming that in both batches the reactants were stoichiometrically balanced, did both reactions go to completion? Explain.

No. For $p \to 1$, $\frac{M_w}{M_n} \to 2$, and for Batch A $M_w/M_n = 1.988$, so batch A could be reacted further

For Batch B, $\frac{M_w}{M_n} = 2.00$, so it has gone to completion

2. A monomer with a molecular weight of 100 g/mole is polymerized in solution using benzoyl peroxide as the initiator. The monomer and initiator concentrations are held constant at 3 moles/liter and 0.004 moles/liter, respectively. The rate of polymerization is measured as 1.50 x 10-4 moles/liter•s, and the rate of initiation is known to be 2 x 10-9 moles/ liter•s. Experiments to measure the radical lifetime indicate that the average radical lifetime is 3.5 s. Assume there is no chain transfer.

a) determine the kinetic chain length $\bar{\nu}$.
b) assuming termination occurs only by combination, determine the number average molecular weight M_n of the polymer
c) assuming now that the reaction goes to completion, determine the weight average molecular weight M_w of the polymer.
d) determine the concentration of propagating radicals [P•] (or [M•])
e) determine k_t, the rate constant for termination.

f)

$M_0 = 100$ g/mole

$[M]_0 = 3 \frac{\text{moles}}{\text{liter}}$ $\quad [I]_0 = 0.004 \frac{\text{moles}}{\text{liter}}$

$R_p = 1.50 \times 10^{-4} \frac{\text{moles}}{l \cdot s}$ $\quad R_i = 2 \times 10^{-9} \frac{\text{moles}}{l \cdot s}$ $\quad \bar{\tau} = 3.5\ s.$

a) $\bar{\nu} = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{1.50 \times 10^{-4} \frac{\text{moles}}{l \cdot s}}{2 \times 10^{-9} \frac{\text{moles}}{l \cdot s}} = 75{,}000$

b) $N_n = 2\bar{\nu} = 2(75{,}000) = 150{,}000$

$M_n = M_0 N_n = (100\ g/\text{mole})(150{,}000) = 1.50 \times 10^{7} \frac{g}{mol}$

c) For term. by combin. only,

$\frac{M_w}{M_n} = \frac{N_w}{N_n} = \frac{2+p}{2}$ so $M_w = 1.5(M_n) = 2.25 \times 10^{7} \frac{g}{mol}$

d) $\bar{\tau} = \frac{[P\cdot]}{2k_t[P\cdot]^2} = \frac{1}{2k_t[P\cdot]} = 3.5\ s \rightarrow k_t = \frac{1}{2\bar{\tau}[P\cdot]}$ (known)

$R_i = R_t = 2k_t[P\cdot]^2 = 2 \times 10^{-9} \frac{\text{moles}}{l \cdot s} \rightarrow R_i = 2\left(\frac{1}{2\bar{\tau}[P\cdot]}\right)[P\cdot]^2$

$R_i = \frac{1}{\bar{\tau}}[P\cdot] = 2 \times 10^{-9} \frac{\text{moles}}{l \cdot s}$

$$[P\cdot] = \left(2\times 10^{-9}\ \frac{\text{moles}}{l\cdot s}\right)\bar{\tau} = \left(2\times 10^{-9}\right)\left(3.5\right) = 7.00\times 10^{-9}\ \frac{\text{mole}}{l}$$

e). $$k_t = \frac{1}{2\bar{\tau}[P\cdot]} = \frac{1}{(2)(3.5s)\left(7.0\times 10^{-9}\ \frac{\text{mole}}{l}\right)}$$

$$= 2.041\times 10^{7}\ \frac{l}{\text{mol}\cdot s}$$

f) $$\frac{1}{\bar{\nu}_{tr}} = \frac{1}{\bar{\nu}} + \sum C_{Rx}\frac{[Rx]}{[M]}$$

$$= \frac{1}{\bar{\nu}} + C_S\frac{[S]}{[M]} + C_M\frac{[M]}{[M]}$$

$$= \frac{1}{75{,}000} + \left(3\times 10^{-4}\right)\frac{6}{3} + \left(1\times 10^{-5}\right)\frac{1}{1}$$

$$= 6.233\times 10^{-4}$$

$$\bar{\nu}_{tr} = \underline{1604}\ !$$

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3.

a) A polymerization reaction is stopped after only a few percent of the monomer is converted to polymer. Which of the two main types of polymerization reactions that we studied will give higher M_n. Explain briefly.

Addition / chain growth will have already produced a few chains of very high MW. Since monomer is excluded from the mw calculation for M_n for addition rxns, M_n will be higher.

b) Describe (briefly) two ways of controlling the molecular weight of a polymer produced by step-growth (condensation) polymerization.

- add an excess of 1 of the reagents (e.g. B-B) (stoichiometric imbalance). All chains will be capped by excess group
- stop rxn ~~at~~ before extent of reaction reaches too high a value ($p<1$).
- add a monofunctional reagent.

c) Describe (briefly) two ways of controlling the molecular weight of a polymer produced by chain growth (addition) polymerization.

- add a chain transfer agent. This controls $\bar{\nu}$ as shown in 2f.
- add more initiator, since

$$\bar{\nu} = \frac{k_p[M]}{2(f k_t k_d [I])^{1/2}}$$

- change [M]