Chapter 4 Homework: Polymer Synthesis
Due:
Available points: 50

1. **Compare and Contrast Step Polymerization and Addition Polymerization (14 points)**

	Step	Addition
Growth Mechanism	Reaction/Combination of two oligomers	Addition of monomer to only the end of another longer chain
Monomer Loss	Rapid Loss of monomer Species (dimer created first)	Relatively slow loss of monomer species
Driving Force	Removal of condensation Product	Conversion of 1 double bond to 2 single bonds
Molar Mass Increase Rate	Increases slowly to start, then quickly towards the end	Increases rapidly throughout and is more constant growth rate
End Reactivity	Remains Active	Not active post-termination
Molecular Species Present	Wide range of oligomers of different chain lengths	Contains high MW polymer, monomer, and a small amount of growing chains
Initiator Required?	Not Necessary	Almost always necessary, and must be activated to combine with monomer

2. **Circle the correct answer. Carothers' Theory is only valid for which type of polymerization? (1 point)**

   a. Step
   b. Radical
   c. Ionic
   d. Photopolymerization
   e. All of the above

3. **Circle the correct answer: Which is NOT a phase of polymerization? (1 point)**

   a. Initiation
   b. Propagation
   c. Chain Transfer
   d. Termination

4. **Circle the correct answer: What is a chain transfer reaction? (1 point)**

   a. Reaction between two free radicals
   b. Reaction of free radical and ionic species
   c. Reaction that propagates forever until it is terminated on purpose
   d. Reaction where a free radical is handed to the partner molecule and free radical reactions starts from this new molecules
   e. Reaction where a free radical transfers in a chain-like manner.

5. **Circle the correct answer: Which of the following is a characteristic of ionic polymerization? (1 point)**

   a. Ionic polymerization is slower than free radical polymerization
   b. Termination via coupling between two growing chains cannot occur in ionic polymerization because the like charges repel each other
   c. Counterions are only introduced at the end of a reaction to terminate growing chains
   d. ✓ Ionic polymerization is less monomer specific than radical polymerization therefore most polymers are synthesized by ionic polymerization.

6. **Circle the correct answer: Which of the following is NOT a termination mechanism? (1 point)**

   a. Coupling
   b. Disproportionation
   c. Chain Transfer
   d. All of the following are termination mechanisms

7. **Quantify the effect of the increase in monomer concentration and initiator concentration:**
   a. **Rate of propagation in an equation (1 point)**

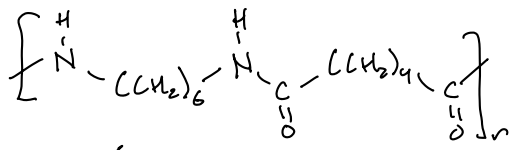
$$R_p = k[I]^{1/2}[M]; \quad [I]\uparrow \Rightarrow R_p \uparrow, \quad [M]\uparrow \Rightarrow R_p \uparrow$$

   b. **Degree of polymerization in an equation (1 point)**

① Disproportionation: $X_n = \frac{[M]}{[I]^{1/2}}$ ② Coupling: $X_n = 2\cdot\frac{[M]}{[I]^{1/2}}$; $[I]\uparrow \Rightarrow X_n \downarrow$, $[M]\uparrow \Rightarrow X_n \uparrow$

8. **Indicate the effect (increase or decrease) of changing the monomer or initiator concentration on the rate of propagation and degree of polymerization in the following situations (4 points)**
   a. Increase [M]
      Rate of Propagation: ↑ Degree of Polymerization: ↑
   b. Increase [I]
      Rate of Propagation: ↑ Degree of Polymerization: ↓
   c. Decrease [M]
      Rate of Propagation: ↓ Degree of Polymerization: ↓
   d. Decrease [I]
      Rate of Propagation: ↓ Degree of Polymerization: ↑

9. Calculate the feed ratio (ratio of the number of initial monomers) of adipic acid and hexamethylenediamine that should be employed to obtain nylon-6,6 of approximately 10,000 g/mol at 99.95% conversion. Show all your work including formulas to receive full credit. Report answer to 4 sig figs. (6 points)

Nylon-6,6: 

$M_n = 10{,}000$ g/mol $\rightsquigarrow$ $M_n = X_n * (\text{Repeat Unit weight})$

$p = 99.95\% = 0.9995$

$X_n = \frac{1+r}{1+r-2rp}$; solve for $r = \frac{N_A}{N_B}$ ← Feed Ratio

Nylon-6,6 Repeat Unit Weight

C: 12.011 g/mol
H: 1.0089/mol
N: 14.0079/mol
O: 15.999 g/mol

$MW_{RU} = 10(CH_2) + 2(\overset{O}{\overset{\|}{C}}) + 2(\overset{H}{N})$

$= 10(12.011 + 2(1.008)) + 2(12.011 + 15.999) + 2(14.007 + 1.001)$

$= 226.306$ g/mol

$X_n = \frac{M_n}{MW_{RU}} = \frac{10000 \text{ g/mol}}{226.306 \text{ g/mol}} = 44.188$

Calculate r using general curve eq

$X_n = \frac{1+r}{1+r-2rp}$

$44.188 = \frac{1+r}{1+r-2r(.9995)}$

$= \frac{1+r}{1+r-1.999r}$

$= \frac{1+r}{1-0.999r}$

$44.188 - 44.1438r = 1+r$

$43.188 = 45.1438r$

$r = \frac{43.188}{45.1438} = 0.9567$

$\boxed{r = 0.9567}$

10. Describe the four steps of the Trommsdorff-Norrish effect. (4 points)

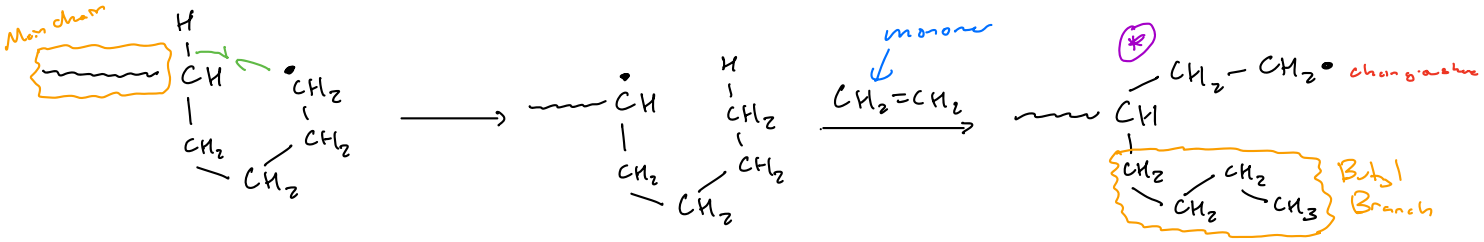
(i) As the content of large polymer molecules increases with reaction time and the polymer solution eventually gels, the viscosity of the solution dramatically increases.

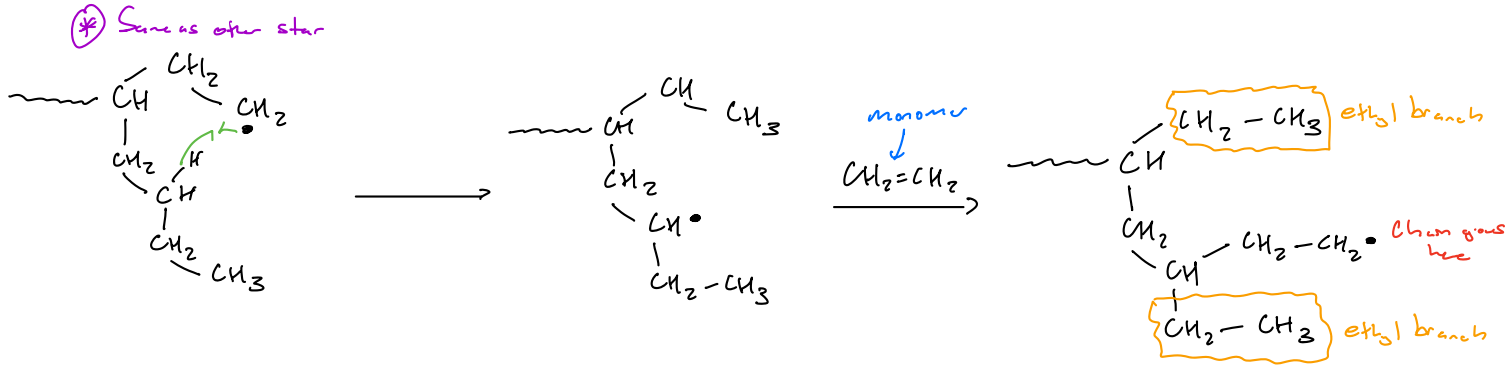
(ii) The mobility of the polymer chain radicals nearly halts and hence k_t is reduced substantially due to the low diffusion rates of the polymer free radicals in such viscous media. In the meantime, the initiator molecules continue to split. Thus, the steady-state condition no longer holds.

(iii) The small monomer molecules can easily diffuse to the polymer free radicals as well as the usual initiator free radicals.

(iv) From the overall rate equation, a reduction in k_t increases both R_p and X_n, which are the rate of propagation and degree of polymerization, respectively.

11. Draw the back-biting mechanism. Indicate the main chain direction and label the type of branching (8 points)





12. Fill in the Blank (3 points)

a. Short-chain branching is an Intramolecular chain transfer mechanism. Short-chain branching in polyethylene is known as Back-Biting, resulting in ethyl and butyl branches. The net free radical concentration does not (does/ does not) change.

13. Define the following terms and draw a graph comparing the two. Make sure to label the axes and corresponding lines. (4 points)

a. Inhibitor – Agents that prevent radical polymerization by reacting with the initiating and propagating radicals. They convert these molecules into non-radical species or radicals of low reactivity too low to undergo propagation.

b. Retarder – Agents that slow radical polymerization by reacting with a fraction of the initiating and propagating radicals