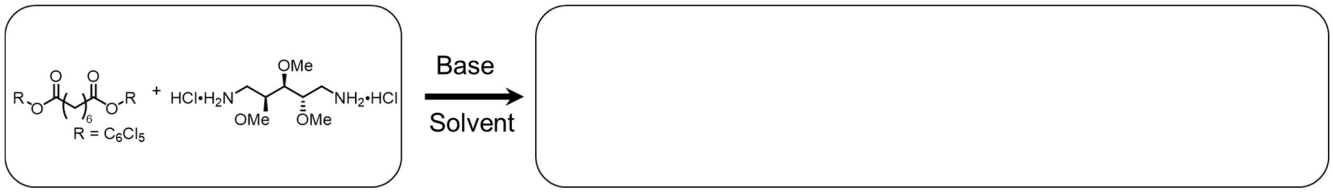
Question 1: Synthesis, Structure, and Macromolecular Properties (20 pts)
The following macromolecules have been recently reported in the chemical literature.



Monomer Structure *Polymer Structure*

Galbis and coworkers. *Macromolecules*

a) In the box provided, fill in the polymer structure that would be expected from this reaction. (2 pts)

b) Propose a mechanism for how the polymerization proceeds. Showing the mechanism may only require showing a fragment of the polymeric structure. (2 pts)

c) Why is it necessary to start with the activated Aldaric acid? What qualitative differences in the rate of polymerization and molecular weight would you expect if you instead used the free carboxylic acid? (2 pts)

d) The melting temperature (T_M) as measured by differential scanning calorimetry is shown to be 210 °C. What does the presence of a melting temperature indicate? Rationalize this observation and show a structural diagram to help explain your observation. (2 pts)

e) If a stereochemically irregular diamine was used, what do you predict would happen to the T_M? Explain your rationale. You may want to show a chemical structure to explain your reasoning. (2 pts)

f) What do you predict would happen to the T_M if a longer alkyl spacer was used in the diester? Explain your rationale. You may want to show a chemical structure to explain your reasoning. (2 pts)

(This question is continued on the next page)

Monomer Structure A *Monomer Structure B* *Polymer Structure*

Watson and coworkers. *Journal of Polymer Science*

g) In the boxes provided, fill in the polymer structure that would be expected from this reaction. (2 pts)

h) Using the Carothers equation, predict the degree of polymerization for varying comonomer compositions (assuming complete conversion) given below. Show the equation you used to determine these values. (2 pts)

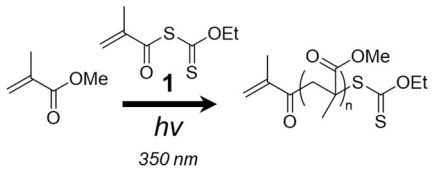
Feed Ratio (9:10 **A:B**):
Feed Ratio (12:13 **A:B**):
Feed Ratio (13:12 **A:B**):
Feed Ratio (99:100 **A:B**):

i) Differences in structure arise when swapped co-monomer ratios, (22:20 **A:B**) versus (20:22 **A:B**), are used. Draw chemical structures of the most probable structure of these two reactions and propose an experimental approach to differentiate between these two structures. (2 pts)

j) You find that when attempting to synthesize longer polymer structures (*e.g.* degree of polymerization > 100), the predicted and observed degree of polymerization differ significantly. Propose an explanation for this observation and a method to characterize the molecular weight of these systems, detailing how the data is interpreted. (2 pts)

Question 2: Photoinitiated Polymerization of Complex Polymer Architectures (20 pts)

Writing in *J. Am. Chem. Soc.* Francis and coworkers reported the use of an iniferter strategy that relies on a *S*-methacryloyl *O*-ethyl xanthate derivative (**1**) and enables exquisite polymerization control over methyl methacrylate polymerization. This photoinitiated polymerization uses 350 nm light and proceeds at room temperature efficiently.



(a) Propose a mechanism for the photoinitiated polymerization of this macromolecule. Note that the first step is photoexcitation of **1**, which leads to a semi-persistent organic radical. Using your mechanism, account for the chain ends of the resultant polymer. *Hint: Termination events should be explicitly shown.* (5 pts)

(b) Your advisor asks you to use this approach to synthesize high molecular weight macromolecules. Your senior lab mate suggests that to obtain high molecular weights (>1000 g mol^{-1}) using this method, you will need to run this polymerization to extremely high conversion. Is this correct? Why or why not? (5 pts)

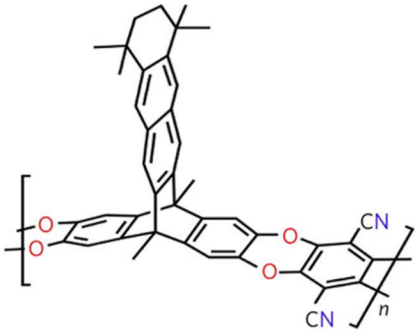
(c) After some experimentation, you achieve high molecular weights using this approach. Your senior lab mate suggests that heating the reaction will help reduce the reaction time. First, this lab mate gives you 1-bromonapthalene (b.p. 135 °C) and suggests running it at reflux, which leads to only minor conversion (5%>). They then suggest running it at reflux in sulfolane (b.p. 285 °C), which leads to no observable polymerization. Suggest reasons why these two reactions failed (*hint: the reasons may not be the same*). (5 pts)

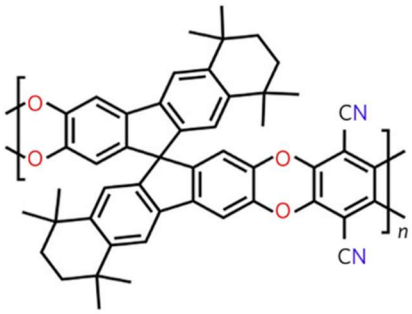
(d) Using the same xanthate-containing photoinitiator for the polymerization of styrene leads to extraordinarily branched polystyrene. Propose a mechanism for the formation of hyperbranched polystyrene. (3 pts)

(e) Rank the amount of expected branching for the following compounds: styrene, 4-dimethylaminostyrene, 4-methoxy styrene, and 4-cyanostyrene. Justify your selection. (2 pts)

Question 3: Polymers of Intrinsic Microporosity (20 pts)

McKeown and coworkers recently reported experimental observations that showed some linear polymer structures were well-suited to perform gas separations.



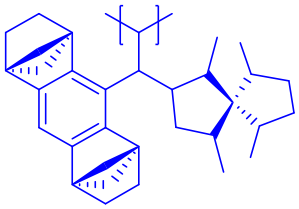


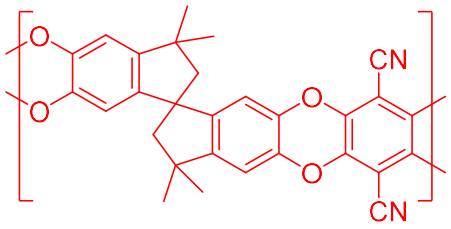
(a) Propose monomer structures and reactions conditions to produce each of the polymers shown above (2 pts).

(b) Show the mechanism of polymerization for the second polymer, which is known as PIM-1. (3 pts)

(c) You perform these polymerizations with new conditions and observe higher gas separation efficiencies than those previously achieved by the same polymers produced through other conditions. You submit your findings to *J. Am. Chem. Soc.* and during review, a reviewer suggests that you may not have performed the polymerization at all. Instead, they suggest you have reduced your nitriles to amines and cocrystallized those with catecholates produced through an unspecified degradation mechanism. What characterization can you do to evaluate this possibility? Be specific about what you intend to observe (or not observe) in your proposed experiment(s). (5 pts)

(d) Strategies to produce polymers of intrinsic microporosity from free radical polymerization and condensation polymerization have both been proposed (though one of these routes has not yet been realized). Label the two structures below as to which is formed from a "chain-growth" and which is formed from a "step-growth" polymerization. (2 pts)





(e) Draw a general plot of molecular weight (Y axis) versus monomer conversion (X axis) for each of these types of polymerizations (chain growth vs step growth). Discuss briefly the origin of the shape of these curves of molecular weight versus conversion. (8 pts)

Question 4: Hydrogen-Bonding Interactions in Macromolecules (20 pts)

Poly(ε-caprolactone) and poly(ε-caprolactam) are two very similar chemical structures. Poly(ε-caprolactam is one of the most widely produced industrial polymers whereas poly(ε-caprolactone) is produced in far smaller quantities.

(a) The T_g of poly(ε-caprolactone) and poly(ε-caprolactam) are -60 °C and 52 °C, respectively. The T_M of poly(ε-caprolactone) and poly(ε-caprolactam) is 60 °C and 227 °C, respectively. Briefly explain the difference observed between these two polymers mechanical properties and draw a molecular structure diagram that explains the significant differences. (4 pts)

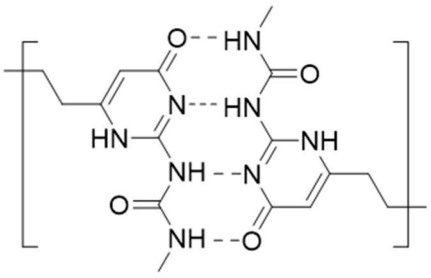
(b) Propose an AA – BB condensation polymerization (i.e. two monomers) for both poly(ε-caprolactone) and poly(ε-caprolactam). Note the relevance of any supporting reagents you propose and justify your solvent selection. (4 pts)

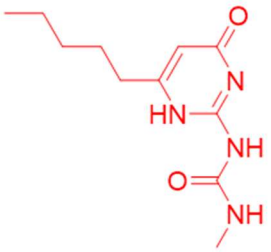
(c) After attempting the AA-BB condensation polymerization several times, you recognize that this route does not allow for the high molecular weights you aimed to obtain. After running ^{1}H NMR on your reaction mixture, you find that you have a 5% excess of one of your monomer species. Rationalize how this observation explains the low molecular weights you are observing. (2 pts)

(d) What could be done to perform a precisely balanced stoichiometric polymerization with an AA and BB monomer? (2 pts)

(e) Another approach to synthesizing high molecular weight poly(ε-caprolactone) and poly(ε-caprolactam) is to use an AB polymerization, which is inherently stoichometrically balanced. Assume you run this polymerization to 95% conversion. If you perform MALDI-MS on both these polymers, what would you expect to find as the most intense peak for both polymers? What splitting between the next most probably peaks would you expect? Assume both polymers are proton terminated. (4 pts)

(f) Nature uses H-bonding motifs to produce materials that are strong, but dynamic. This has recently inspired a variety of synthetic designs to produce supramolecular polymers, which are linked through non-covalent bonds, that mimic this behavior. You decide to reproduce previously reported materials with these motifs (shown below). Instead of a strong solid, you isolate a goopy gel. You realize your starting monomers were contaminated with the species shown in red. Why is your material different than previously reported systems? (2 pts)

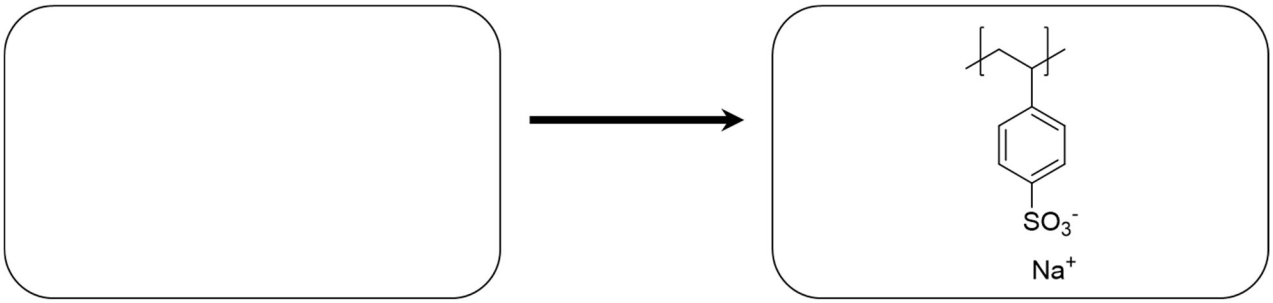




(g) Next, you attempt a postsynthetic polymerization on your supramolecular polymer but when subjecting your polymer to DMF, you realize you no longer isolate any macromolecular material. Propose a hypothesis for this observation. (2 pts)

Question 5: Polymers in Medicine

Polystyrene sulfonate (PSS, structure shown below) is administered as its sodium form to treat a variety of liver and kidney disorders. This polymer has the effect of treating hyperkalemia (elevated blood K^+), which can lead to cardiac arrest. However, it sometimes has the unintended side effect of reduced bone density. The polymeric structure of PSS prevents it from passing intestinal barriers (and prevents it from entering bacteria in the gut fauna).



Monomer Structure *Polymer Structure*

(a) Propose a monomer species and synthesis to prepare PSS. Hint: *this polymer cannot be directly polymerized from its repeat unit.* (2 pts)

(b) Assume that you thermally initiate the polymerization shown above with AIBN and terminate by H abstraction. Show all of the operative mechanisms for each the fundamental steps (initiation, polymerization, and termination) for this polymerization. (3 pts)

(c) Show the chemical structure of the polymer (with chain ends and degree of polymerization) you would obtain assuming the following conditions. Assume you always initiate using AIBN. Show your work. (10 pts)

Recall that the kinetic chain length produced through termination by H atom abstraction can be defined as:

$$Kinetic\ Chain\ Length = \frac{R_p}{R_t} = \frac{k_p[M]}{(f k_i k_t [I])^{0.5}}$$

$f = 1.0$
Rate of polymerization = $1.65 \cdot 10^{-3}$ L mol^{-1} s^{-1}
Rate of termination by H-atom abstraction = $6.0 \cdot 10^{-7}$ L mol^{-1} s^{-1}
Rate of termination by combination = $3.0 \cdot 10^{-6}$ L mol^{-1} s^{-1}
Rate of initiation by AIBN = 0.165 L mol^{-1} s^{-1}
[M] = 2 M
[I] = 0.15 M

Assuming H-atom abstraction termination:

Assuming termination by combination:

Assuming you double the monomer concentration and terminate through abstraction:

Assuming you increase the initiator concentration by 25X and terminate through abstraction:

Assuming you change the solvent and terminate through combination, which doubles the rate of initiation and increases the rate of polymerization by 10X.

(d) Propose an explanation for what occurs to this polymer as it enters the acidic stomach environment (pH = 2.0) and then the ionic environment of the intestines. How does this explain the desired outcome and unintended side effects of PSS treatment (described at the beginning of this question). (5 pts)