Question 1: Polymer Product Reverse Engineering (20 pts)
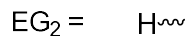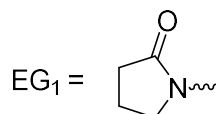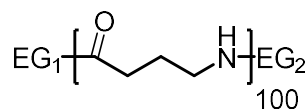
Your boss calls you into their office and informs you that a competitor's product is poised to disrupt the polymer market that your company currently dominates. Fortunately, your competitor's product is not patent protected. Your boss overheard from a former employee of the company that the product is a polyamide with the structure shown below. Unfortunately, you don't know other features (e.g. dispersity, chain end identity) of the material. Now, you must prepare some polymers for subsequent testing to determine what polymer your competitor is using. You begin by planning to synthesize the following two test systems.

Propose a complete synthesis (solvent, moles/equivalents of reagents, steps) for the following polymer (10 pts):

$$EG_1 \left[\begin{array}{c} O \\ \| \\ \end{array} \quad \begin{array}{c} H \\ N \\ \end{array} \right]_{100} EG_2$$

EG$_1$ =

EG$_2$ =   H〰

Dispersity = 1

Propose a complete synthesis (solvent, moles/equivalents of reagents, steps) for the following polymer (10 pts):
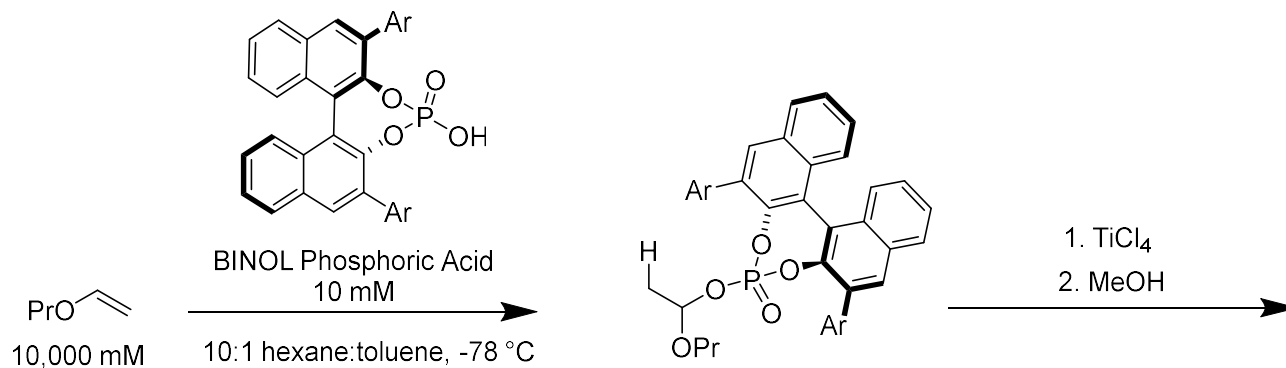

$EG_1 = $ Cl⁓

$EG_2 = $
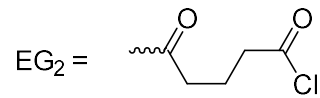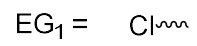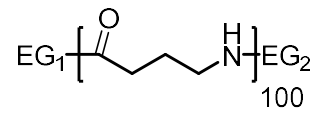
Dispersity = ≥2

Question 2: Irreproducibility in the Lab (20 pts)

Your PI calls you three years after you graduate and explains that a trainee in the lab is unable to reproduce results you published while you were completing your PhD. The synthetic scheme you reported is shown below.

Propose a mechanism for the TiCl$_4$ mediated polymerization. Using this mechanism, indicate the resultant polymer structure that will be obtained from this polymerization, accounting for the chain ends, molecular weight, and dispersity of this structure. (10 pts)

After speaking with the current graduate student, you find that the main observable difference is that they are isolating a low viscosity gel instead of a hard solid. After some discussion, you find that they are using a racemic BINOL derivative to prepare their phosphoric acid because it is much cheaper than the enantiopure reagent you used, which they highlight several times in your discussion. Unfortunately, they have emailed you (and your former PI) before collecting any characterization data. Propose a reason the racemic BINOL derivative leads to a difference in the observed properties of the polymer they isolate versus the one you isolated. (3 pts)

Propose a characterization method that could be used to determine if your hypothesis is accurate and explain how it should be interpreted. (2 pts)

A month later, the graduate student calls you again to inform you that even when they switched to the enantiopure BINOL (which is much more expensive than the material they were using) derivative, they still can't isolate as hard of a solid as you were able to isolate! After some discussion, you realize that they changed the solvent conditions to include a more polar solvent. The graduate student explains that this makes the polymerization much faster - taking the polymerization time from 1 minute to 5 seconds. Propose a hypothesis for why this solvent change increases the reaction rate but diminishes the mechanical strength of the obtained polymer. (5 pts)

Question 3. Ionicity in Polymer Chemistry (20 pts).

Propose reasonable synthetic conditions to access the following polymer structure. (5 pts)
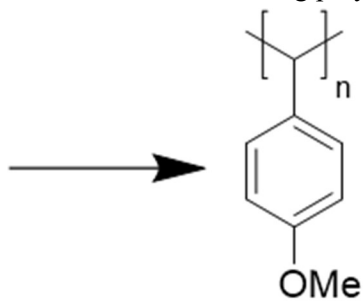
Show the initiation, propagation, and termination steps associated with the polymerization conditions you have proposed. (5 pts)

Based on your proposed conditions, identify reasonable chain ends of your polymer. (2 pts)

Your advisor suggests that polymerizing (*p*-dimethylamino)styrene using the same conditions should also work because dimethylamine is a stronger activating group than methoxy. Explain why or why not this logic is correct. (3 pts)

Clearly identify which of the following monomers can be polymerized by cationic methods, anionic methods, or both. Under the reaction arrow of each polymer, predict the polymer structure obtained by ionic polymerization. It is **not** necessary to specify the end groups, dispersities, or molecular weights. (5 pts)
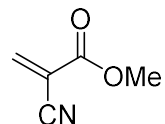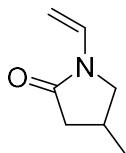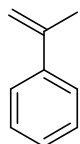
## Question 4. Networks, Vitrimers, and CANs (20 pts).

You are a brand new PI at an R1 university excited to perform their first polymerization in their new lab. You decide to perform the polymerization shown below. Unfortunately, the dynamic nature of transcarbonation exchange reactions allows you to only access a conversion of 90%.
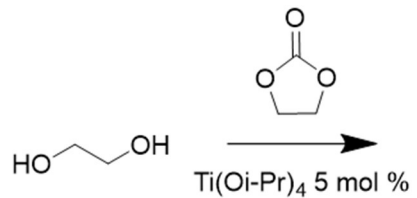
Propose the polymer structure you would expect from the polymerization shown above. You do not need to specify chain ends or molecular weight. (2 pts)

What molecular weight would you expect to access from this polymerization assuming that the two reagents are perfectly stoichiometrically balanced? (3 pts)

You recall from your excellent graduate polymer chemistry class, "The Organic Chemistry of Polymers", that even low conversions can produce network polymers. This leads you to conduct the following polymerization:
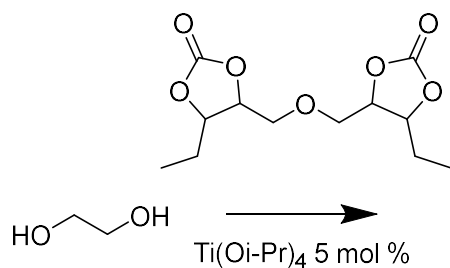
Propose a reasonable network structure that results from this polymerization. Assume stoichiometrically balanced monomers. (3 pts)

Propose a percent conversion that is required to achieve the gel point of this polymerization using the reduced Carother's equation (shown below). (2 pts)

$$\rho_c = \frac{2}{f_{avg}}$$

Propose a reasonable mechanism for the polymerization shown above (5 pts).

After successfully synthesizing and polymerizing this gel, you decide to explore its mechanical properties. To your surprise, you find that at elevated temperatures this polymer network (thermoset) relieves stress like a linear plastic (thermoplastic). Propose a chemical hypothesis, using chemical structure diagrams, to explain this observation. (3 pts)

At elevated temperatures in a non-nucleophilic solvent, the polymer network swells but does not dissolve. Does this indicate that operative transcarbonation processes are associative or dissociative? Explain your reasoning. (2 pts)

Question 5. The Unusual Case of Polysiloxanes (20 pts).

Polysiloxanes, like dimethylsiloxane [-Si(CH3)2O-], is one of the most studied polymers in existence. However, many fundamental properties of polysiloxanes remain unclear such as: (1) why flexible polysiloxanes form crystalline phases, (2) why thermodynamic phase segregation occurs in some polysiloxanes, especially those that contain cyclic motifs, (3) why polysiloxanes exhibit uncharacteristically low bulk viscosity, (4) why the entropies of dilution in solvent is lower than can be explained by theory, and (5) how the interaction of stereochemical variability impacts resultant polymer properties. Despite these limitations, polysiloxanes are used extensively in chemical industry.

Propose a mechanism and polymeric product for the following polymerization (5 pts).
Hint: Toluene is hygroscopic.
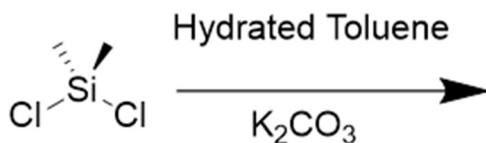
Using your proposed mechanism, account for and identify the following products that you can only identify via mass spectrometry. Assuming a +1 ionization state allows you to extract the following masses. The counterion has already been subtracted from the observed mass. (5 pts)
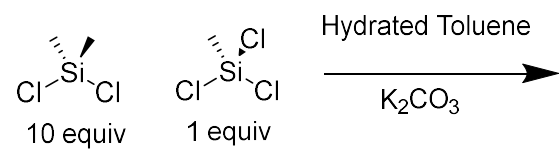
$[M^+] = 222.06$

$[M^+] = 296.08$
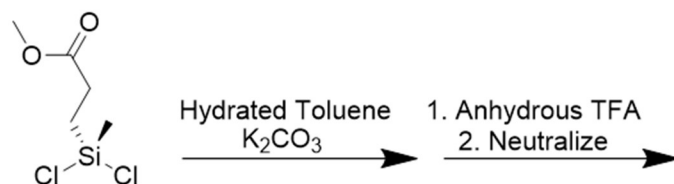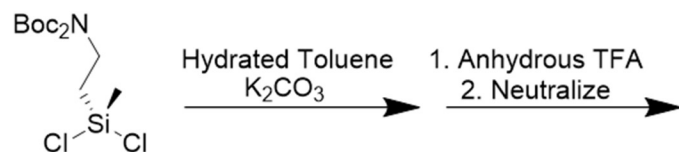
$[M^+] = 370.09$

$[M^+] = 444.11$

Assuming no cyclization occurs during this polymerization, propose a product for the following polymerization. (3 pts)

Using the reduced Carother's equation, predict the percent conversion required to reach the gel point of this siloxane network. (2 pts)

$$\rho_c = \frac{2}{f_{avg}}$$

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Polymerizing the two silanol derivatives shown below and then physically mixing in equimolar ratios them leads to a much harder polymer than either of the two original species. Propose a structure of the polymer mixture. (3 pts)

Boc$_2$N

Hydrated Toluene K$_2$CO$_3$ → 1. Anhydrous TFA 2. Neutralize →

Physically Mix →

Hydrated Toluene K$_2$CO$_3$ → 1. Anhydrous TFA 2. Neutralize →

Propose a rationale for why this physical mixture of polymers is tougher, more hygroscopic, and more adhesive (all qualities that are useful in cosmetics) than either of the parent polymers. Please use a chemical diagram to illustrate your rationale. (2 pts)