Full Name _____

CHM 5275

Organic Chemistry of Polymers

University of Florida
Department of Chemistry

Exam 3
December 6th, 2022

THIS EXAM IS NOT TO BE COPIED IN ANY FORM. SHARING OR COPYING THIS EXAM WILL RESULT IN AN IMMEDIATE ZERO.

This exam is to be completed outside of regularly scheduled class hours. This exam must be returned to Professor Evans (Office LEI402) before 3 pm on December 13th, 2022. Exams turned in after this time will be given an automatic zero. Please write and draw as clearly as possible in the space provided. Answers given outside of this packet will not be graded. If you require additional space and continue an answer on the back of a page, you must clearly indicate this to the grader. There are *no* restrictions on the resources you may use to answer the questions below including (but not limited to) the internet, course materials, or working with your colleagues in this course. NOTE: Identical answers will be considered plagiarism and will not be accepted or graded. As such, if you choose to work with your colleagues in this course, it is suggested that you discuss the content but not share answers directly. If you work together, you must note your collaborators below. This exam may not be shared with anyone not enrolled in CHM 5275. Many of these questions are related to or directly taken from the primary literature. It is expected that you will be able to obtain these works independently.

Question 1:	The Science of Polymer Synthesis (20 pts)	_____
Question 2:	Annulative π-Extension (20 pts)	_____
Question 3:	Surface Tethered Polymerization (20 pts)	_____
Question 4:	Synthetic Sequence Control (20 pts)	_____
Question 5:	Spatiotemporal Control in Polymer Synthesis (20 pts)	_____

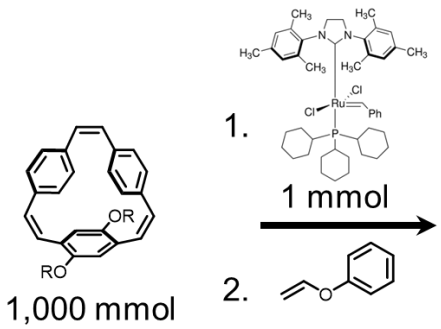
Total Score _____

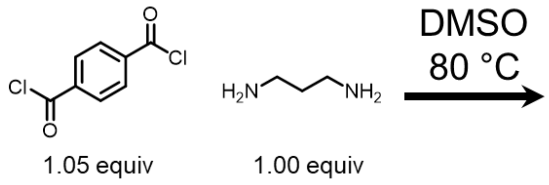
Collaborators: _____

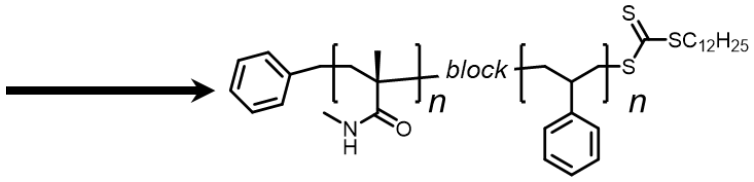
Question 1: The Science of Polymer Synthesis (20 pts)

As a first-year professor preparing their first cumulative exam, you want to test the broad scope of your students' polymer synthetic abilities. You find some previous cumulative exams that you can use as inspiration but the pages are very old and some parts are unreadable.

Propose *either* the (1) conditions and monomer(s) or the (2) polymer structure for each of the following chemical reactions. For all polymer structures you would propose, indicate the molecular weight, dispersity, and end groups you would expect. When noting the polymer structure you would prepare, indicate the stereochemistry, regiochemistry, sequence, and polymer architecture where relevant. (20 pts, 4 pts apiece)



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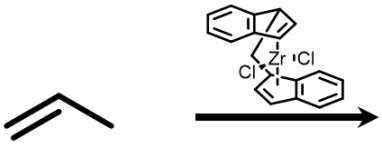
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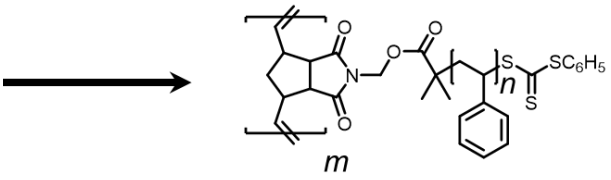
O
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S
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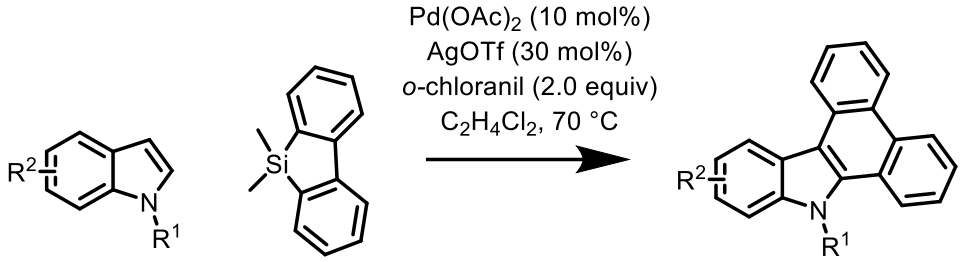
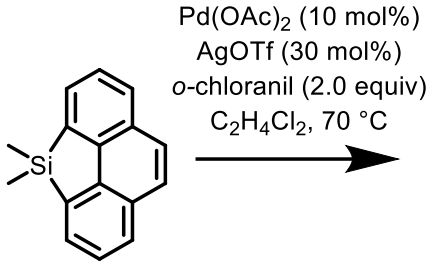
S
SC6H5
m

Question 2: Annulative π-Extension (20 pts)

As a postdoctoral researcher eager to find a faculty position, you are working long days looking for your landmark discovery. To your excitement, you discover an annulative π-extension chemistry that can be used to synthesize the molecular compound shown below.



This is when you have your breakthrough idea – *Could you use this for a polymerization chemistry?* Predict the polymer structure produced by the scheme shown below, being certain to identify the chain ends of this polymer. (5 pts)



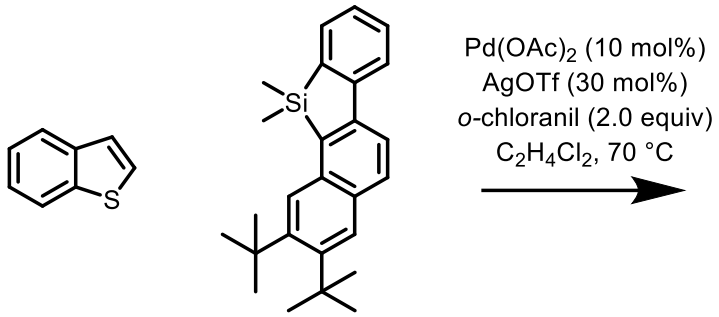
What is the expected Δm/z one would expect to see in MALDI-MS for this polymer chain? (3 pts)

Predict the exact mass you would expect to find here with a degree of polymerization of thirty-five and a charge of +1 (assume that there is no counterion). Show your math. (3 pts)

To your excitement, this mass is observed weakly in MALDI-MS. You attribute the weak intensity to the strong intermolecular interactions between highly aromatic polymer chains. Your advisor asks you to start writing this paper up. Before you do so, she wants to know, should this be considered a step-growth or chain-growth polymerization? (2 pts)

Would this assignment be consistent with the observation of the Dispersity = 1.4 that you observe by GPC? Predict a possible explanation for the low dispersity that you observe. (1 pt)

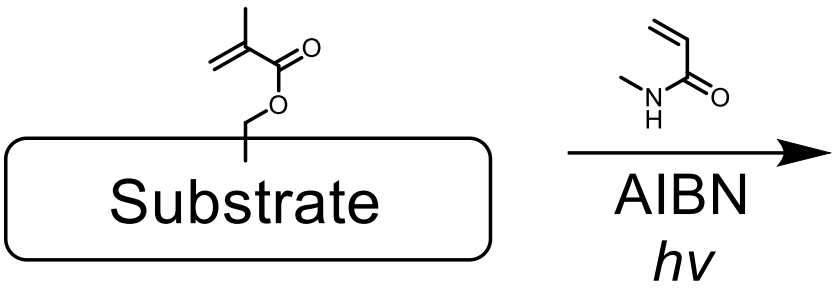
You recognize that the inability to control molecular weight tightly limits your ability to measure the fundamental properties of these unique polymeric materials. Your advisor tells you that if you can identify a way to produce a living polymerization from these structures, you will be certain to get good papers and a great faculty position. So, you go back to the lab and identify a system that should produce a *living* polymerization. Justify why the system below will produce a living polymerization with a mechanism and predict the polymer structure that you would generate from this approach. (4 pts)



The system above behaves exactly as expected, which leads to a highly productive end to your postdoctoral research. As you are looking for faculty jobs, other labs begin emailing you that they are unable to reproduce your mass spectrometry results. Now, questions about the validity of this work begin to spread to the larger chemical community. What chemical technique (and analysis) would you use to support your proposed structures and the MS data you have collected? (2 pts)

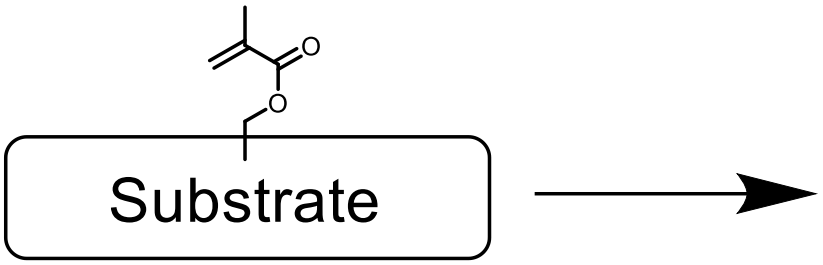
Question 3: Surface Tethered Polymerization (20 pts)

Your chemical company recently purchased a smaller chemical company that is focused on coatings. You're tasked to bring the knowledge from your larger company to this new group. You were led to believe that they were using state-of-the-art methods to produce chemical coatings. They show you the following scheme when you arrive. Predict the polymer structure produced by this polymerization. (5 pts)



Identify two reasons this might not be an ideal polymerization method to produce well-defined coatings. (2 pts)

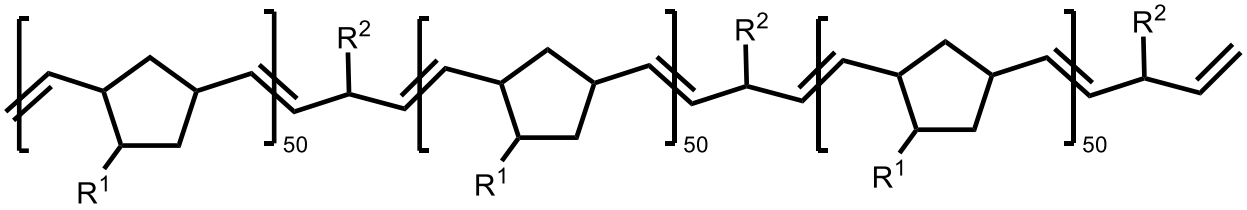
You immediately recognize that variable molecular weights are going to be problematic for coatings (because the surface is then poorly defined). So, you suggest to your team that an ionic polymerization may address this concern. In addition, it will allow you to produce block copolymers, which the group has wanted to do for a great deal of time. Propose a synthetic scheme to access a block copolymer of poly(methyl methylacrylate) and poly(*N*-methylacrylamide), where the polymer is anchored by the poly(methyl methylacrylate) group through the group shown below. (7 pts)



While the coatings prepared through ionic polymerization might be more ideal as coatings, the sensitivity of the reaction conditions makes it challenging to implement them in real processes. You recognize that a controlled radical polymerization might be easier to conduct at scale. Propose a synthetic scheme that takes advantage of ATRP to access polystyrenes of a unimolecular weight that are anchored to the substrate. *Hint: you may want to change the anchoring group, which is connected to a hydroxyl terminated substrate.* (7 pts)

Question 4: Synthetic Sequence Control (20 pts)

Biology is unrivaled in its polymer sequence control. The precise installation of chemical functionality along polymer backbones is an appealing synthetic macromolecular aim. Propose a living polymerization synthetic approach to access the following site-modified polymer structure. *Hint: this polymerization requires the use of Grubb's 2nd generation catalyst.* (3 pts)

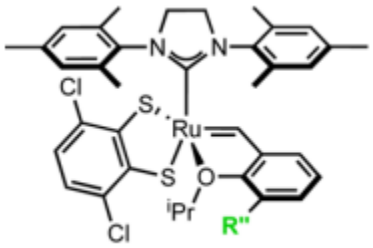


Propose a mechanism for the polymerization you have proposed above. (3 pts)

How would you characterize this polymer structure (not worrying about the exact sequence) demonstrating that you've produced the correct structure? Describe what you would expect to observe with the experiment you proposed. (3 pts)

Many characterization techniques are insensitive to the exact sequence of the polymer structure. Propose an experiment to demonstrate that you have produced an exact molecular sequence. *Hint: you may need to modify the chemical structure of the polymer you propose to demonstrate that you have produced the structure you propose.* (6 pts)

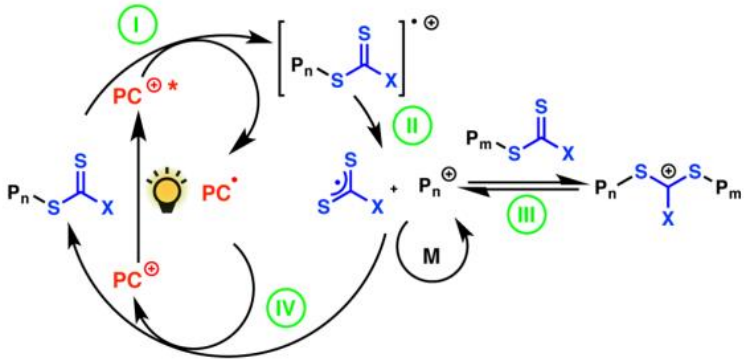
When performing some final experiments to publish this paper, you accidentally use a different Ru pre-catalyst (shown below) than the Grubb's 2 that you have been using. The GPC and MALDI-MS of these polymers are identical to those that you have prepared previously. However, the new properties are much more rigid than the waxy polymers you were preparing previously. This difference leads you to characterize both polymer samples by NMR. The molecular weight (as determined by NMR) matches well with what you anticipate from MALDI-MS and GPC. However, you note something unusual, whereas previously there were two sets of NMR features in the alkene region that were similar intensity, now those features are wildly different in intensity (roughly 100:1). Propose a hypothesis to explain this spectroscopic observation and its relation to the physical properties of this polymer. (5 pts)



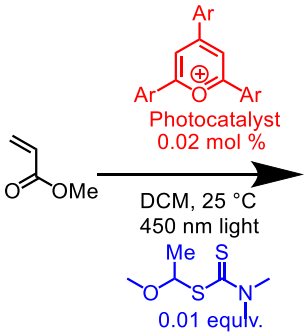
Question 5: Spatiotemporal Control in Polymer Synthesis (20 pts)

The ability to spatiotemporally control polymer molecular weight, molecular weight distribution, and composition would offer new opportunities for high-resolution polymer control. To effectively control polymer structure at this level, external stimuli will be required.

Light is one such external stimuli. The photocatalytic cycle is shown below with PC describing a generic photocatalyst.



Propose a mechanism to explain the polymerization shown below. Be sure to identify the initiation, propagation, termination steps, and how this termination (or better described as reversible addition-fragmentation chain transfer) operates. (4 pts)

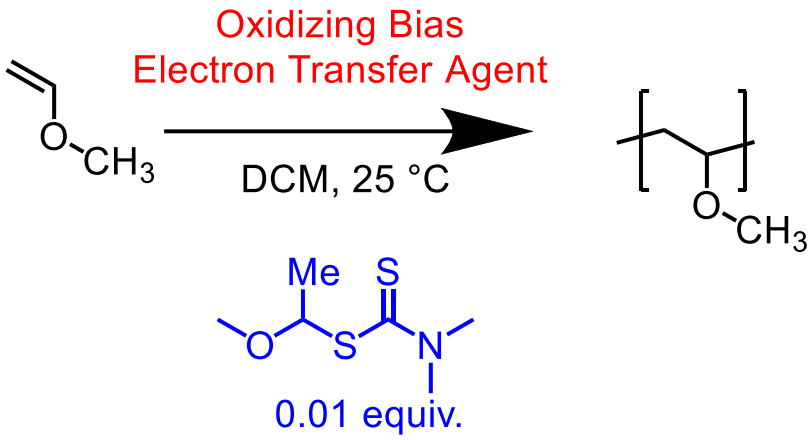


Predict the polymer structure, including degree of polymerization and chain ends, of the following polymerization. (4 pts)

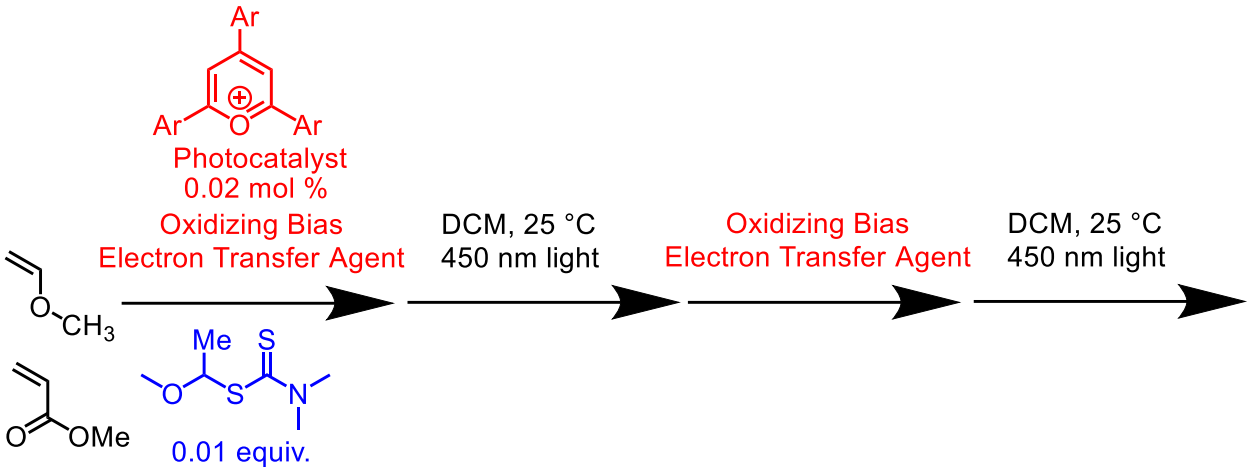
Propose a characterization technique and analysis to prove that you have prepared the polymer structure you intended. (3 pts)

Assuming that this polymerization gives good control of molecular weight and limits the dispersity (i.e. D = 1), what does that indicate about the rates of the processes that you identified below. *Hint.* Specifically, explain how the relative rates of initiation, propagation, and chain transfer (e.g. reversible deactivation) compare to one another. (2 pts)

It turns out that a similar electrochemical stimuli can be employed to polymerize vinyl ethers through a similar mechanism (shown below). Importantly, this stimuli does not allow for the polymerization of acrylates.



Using this knowledge, predict what polymer structure would be produced in the following scheme. (3 pts)


Ar
Ar
O
Ar
Photocatalyst
0.02 mol %
Oxidizing Bias
Electron Transfer Agent
DCM, 25 °C
450 nm light
Oxidizing Bias
Electron Transfer Agent
DCM, 25 °C
450 nm light
O
CH3
Me
S
O
S
N
O
OMe
0.01 equiv.

Propose the characterization you would require to validate your proposed structure. (2 pts)

How would you prove that the polymerization is driven by these external stimuli and not through some other mechanism? Show a representative piece of data to illustrate your proposal. (2 pts)

If you've made it to this point, then you've successfully completed CHM5275. I want to say from the bottom of my heart, I couldn't have had a better first class of students. I hope you feel that this class has better prepared you for your PhD research ahead. Always feel free to swing by my office. I hope I can be as helpful in your journey here at UF and beyond.