

Name: Zac Ahmad (Please write your name on each page)

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Spring 2021 PSC 302 Exam 2 [Total: 100 pts] (Instructor: Patton)

During the exam, no notes, phones (or other electronic devices) or neighborly conversations allowed. You can write on this exam and use extra paper if needed. Please write only on the front side of each paper. Good luck!

1. [3 pts] Which of the following expressions describes the definition of a chain transfer constant? (circle the correct answer)

+3

- a) $k_{tr} \times k_p$
- b) k_{tr} / k_p
- c) $\sqrt{k_{tr}}$
- d) None of the above

2. [3 pts] A substance that reduces the rate and degree of polymerization without completely halting the propagation process, is called a _____? (circle the correct answer)

+3

- a) inhibitor
- b) polymerization modifier
- c) retarder
- d) regulator

3. [3 pts] Which of the following best describes the relative rates for chain transfer and reinitiation for degradative chain transfer? (circle the correct answer)

+3

- a) $k_p \ll k_{tr}; k_a < k_p$
- b) $k_p \gg k_{tr}; k_a \approx k_p$
- c) $k_p \gg k_{tr}; k_a < k_p$
- d) None of the above

4. [3 pts] For a given radical copolymerization of monomer A and monomer B, what does it mean if $r_A < 1$? (circle the correct answer)

+3

- a) $A\cdot$ prefers to add to A
- b) $A\cdot$ prefers to add to B
- c) k_{AA} is larger than k_{AB}
- d) k_{AA} is smaller than k_{AB}

could also be (d)

5. [3 pts] Which of the following pairs of monomers will most likely form an alternating copolymer? (circle the correct answer)

+3

- a) butadiene and acrylonitrile, $r_1 r_2 = 0.0006$
- b) vinyl acetate and diethyl fumarate, $r_1 r_2 = 0.0049$
- c) styrene and acrylonitrile, $r_1 r_2 = 0.016$
- d) butadiene and styrene, $r_1 r_2 = 0.98$

$r_1 r_2 = 0$ means perfectly alternating co-pmr so a is closest

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6. [5 pts] Briefly explain what distinguishes retardation from inhibition.

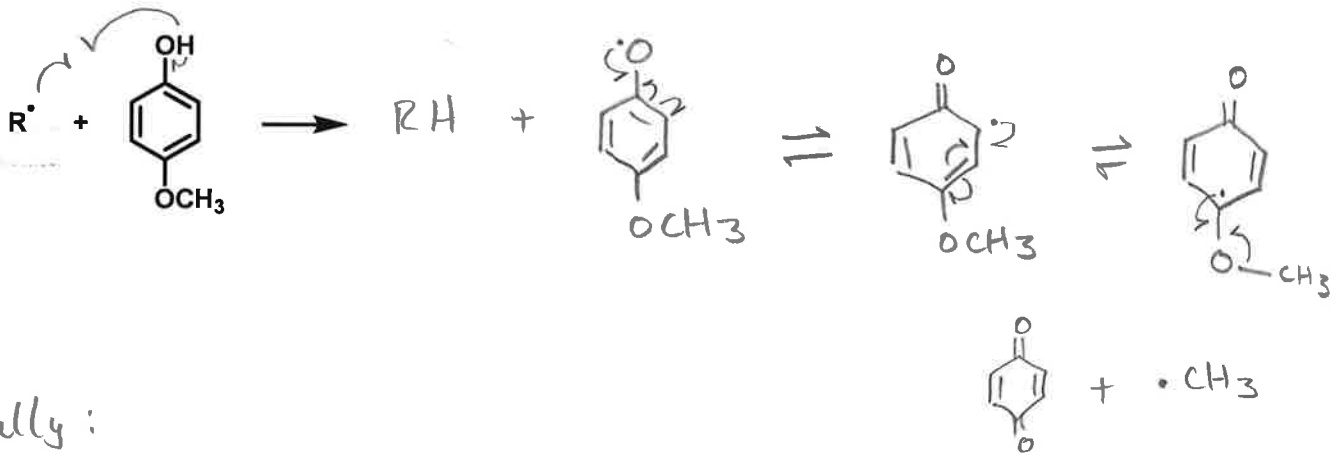
(+5)

Inhibitors react with radicals to effectively halt polymerization until additional monomer is added to continue polymerization. Retarders are not as effective in this regard and only serve to slow the polymerization.

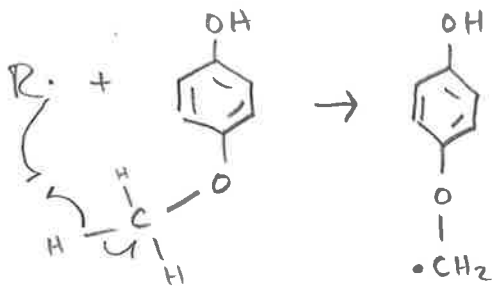


7. [10 pts] Draw the mechanism and all possible products resulting from *p*-methoxyphenol serving as an inhibitor for a generic monomeric radical $R\cdot$.

(+10)



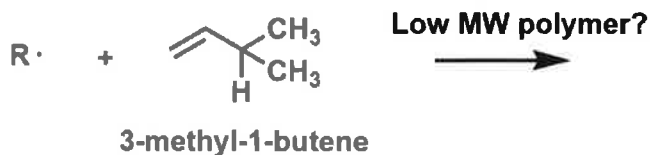
Potentially:



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8. [10 pts] Despite much interest in the monomer 3-methyl-1-butene, thus far, polymer chemists have been unsuccessful in polymerizing this monomer to a significant molecular weight by radical polymerization methods. Postulate why this monomer would be difficult to polymerize and show a mechanism to support your answer.

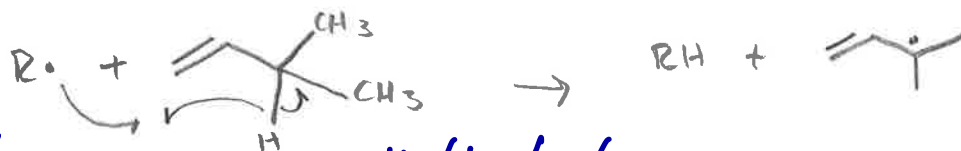
(+9)



I would argue that this is disproportionation of β hydrogens. The radical will not always react with vinylic site which will not promote high MW polymer.



But it can also proceed:



Allylic Radical

yes because \rightarrow allylic hydrogen \rightarrow autoinhibited by monomer

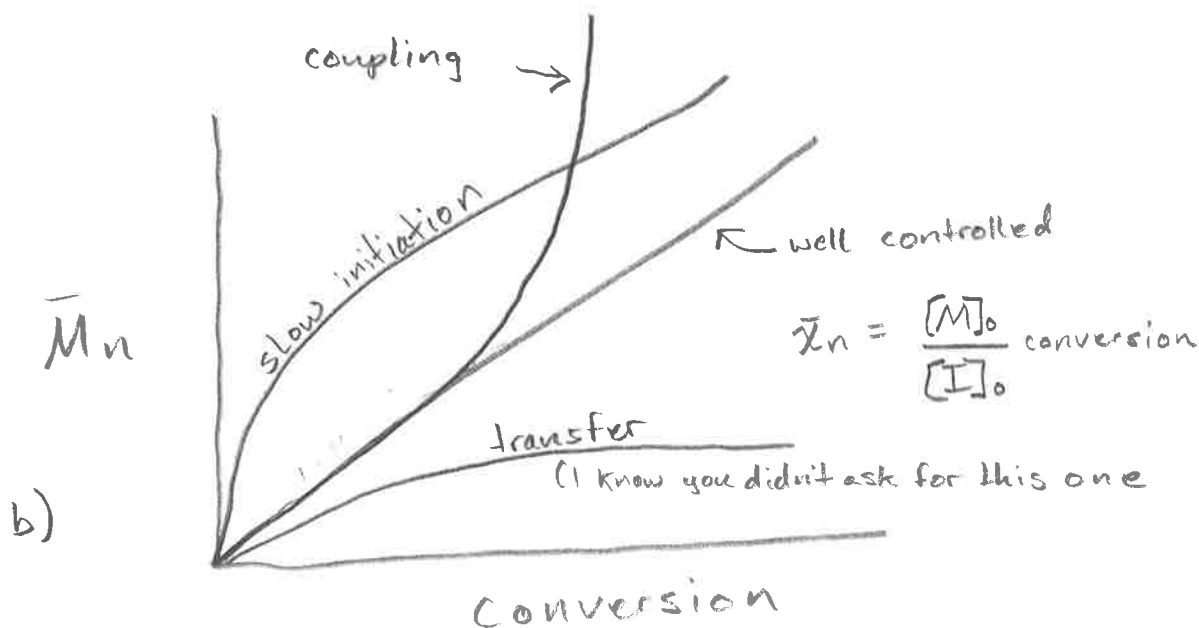
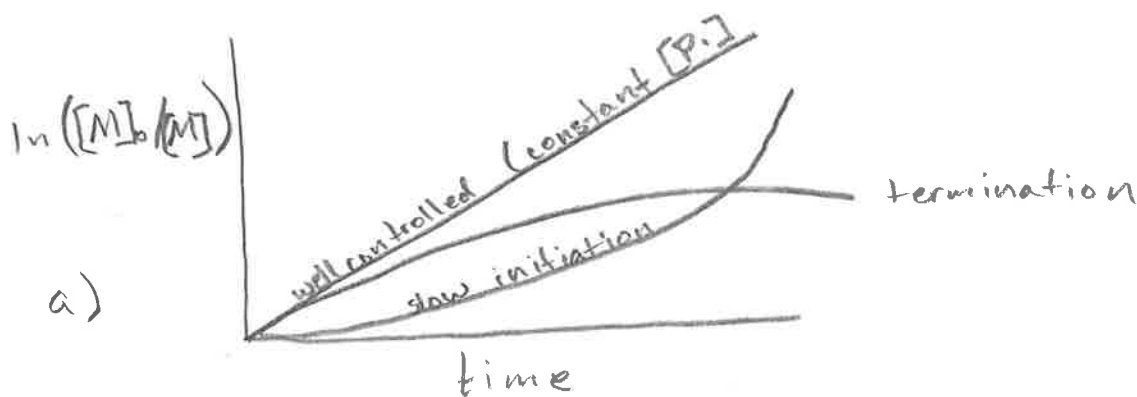
AND possibly



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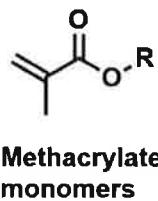
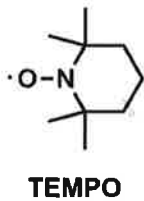
9. [20 pts] Show graphical representations for the following two kinetic features for controlled radical polymerizations (label all axes): (a) **First-order kinetics** (on the same graph, show a curve that represents a well-controlled polymerization, a curve for a polymerization that exhibits slow initiation, and a curve that represents a polymerization that exhibits termination) (b) **Pre-determinable degree of polymerization** (on the same graph, show a curve that represents a well-controlled polymerization, a curve for a controlled polymerization that exhibits slow initiation, and a curve that represents a controlled polymerization that exhibits termination by coupling).



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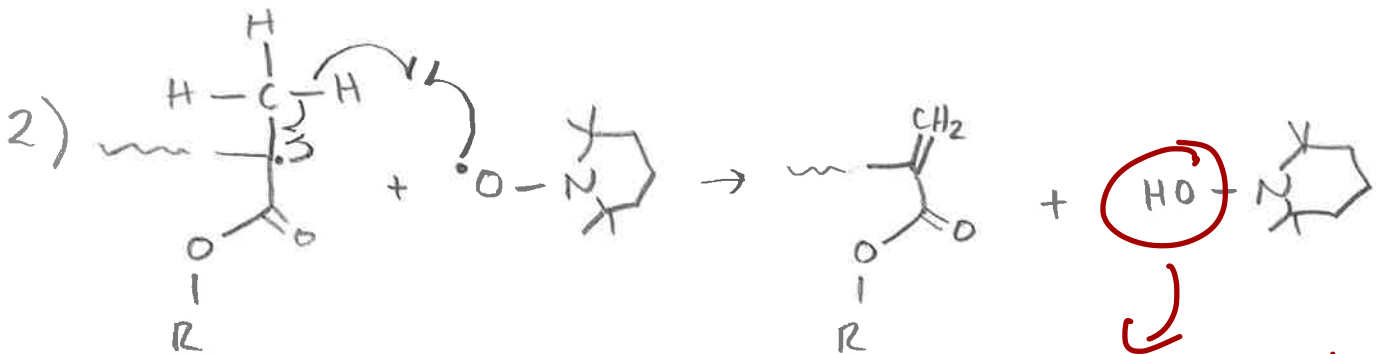
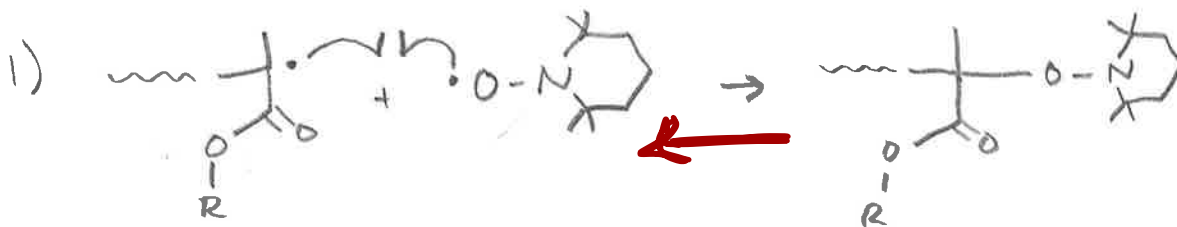
10. [20 pts] Briefly explain the two primary reasons why TEMPO is typically ineffective for controlling the polymerization of methacrylate monomers. Show mechanisms to support your answers. Structures are shown below for reference.

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- ✓ 1. They form sterically bulky products
- ✓ 2. They can cause β hydrogen abstraction

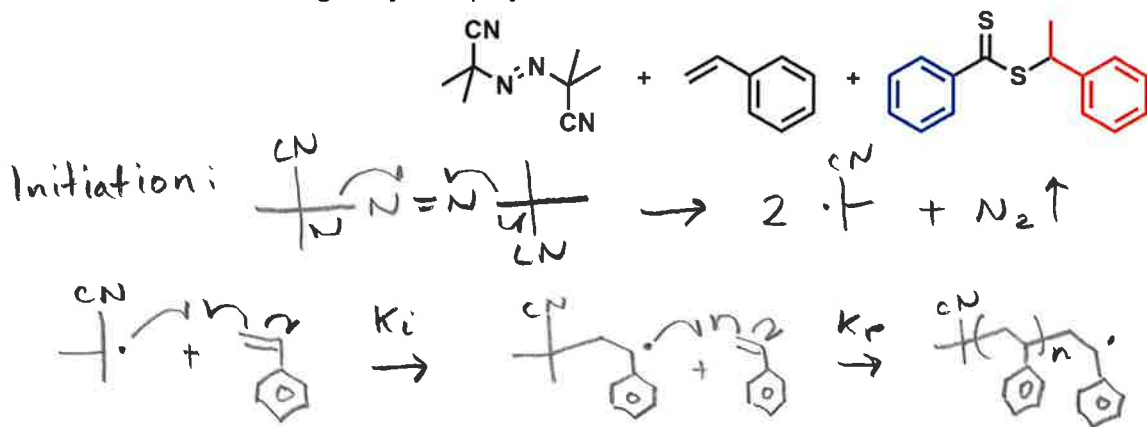
yes, but important to show inference on the add/dest equilibrium



also abstractable hydrogen by prop radical leads to termination

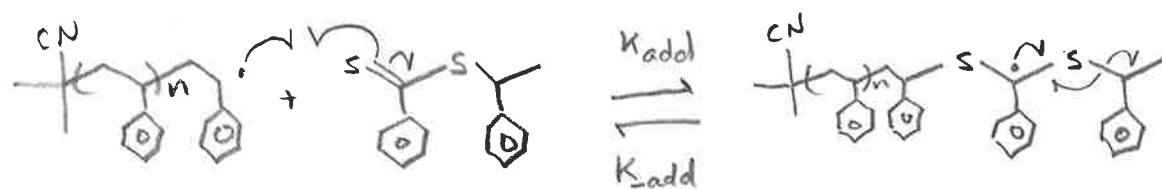
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11. [20 pts] (a) Using the following initiator, monomer, and chain transfer agent (CTA), show the four steps (with mechanisms and properly labeled rate constants) involved in a RAFT polymerization: i) initiation, ii) pre-equilibrium, iii) re-initiation, and iv) main equilibrium. (b) Using the radical addition and fragmentation processes in the pre-equilibrium step, explain whether or not you think the **Z** and **R** groups of the CTA would be effective choices for controlling a styrene polymerization.

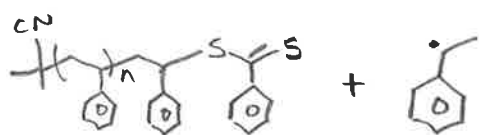


(+4)

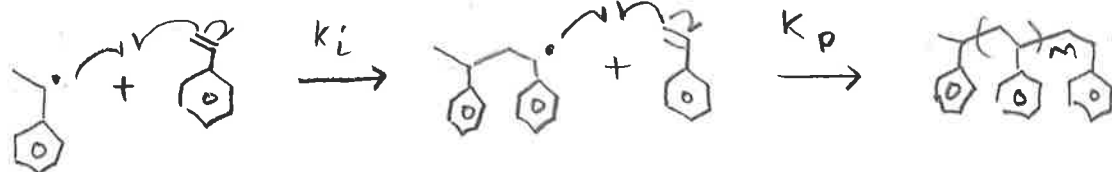
Pre-Equilibrium:



(+4)



Re-initiation:

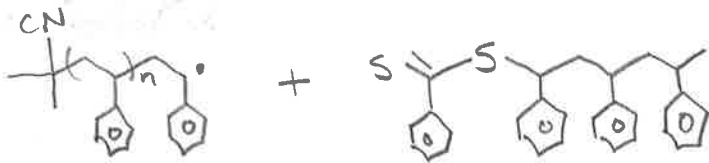
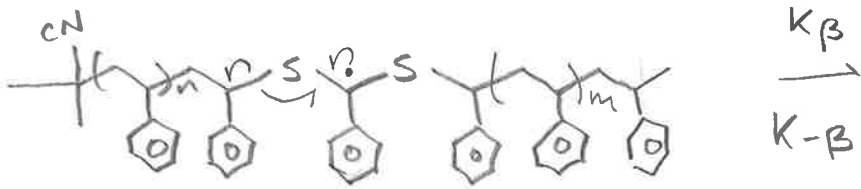
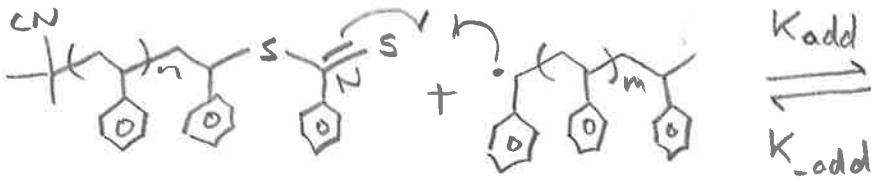


(+4)

11. cont.

(+4)

Main RAFT Equilibrium.

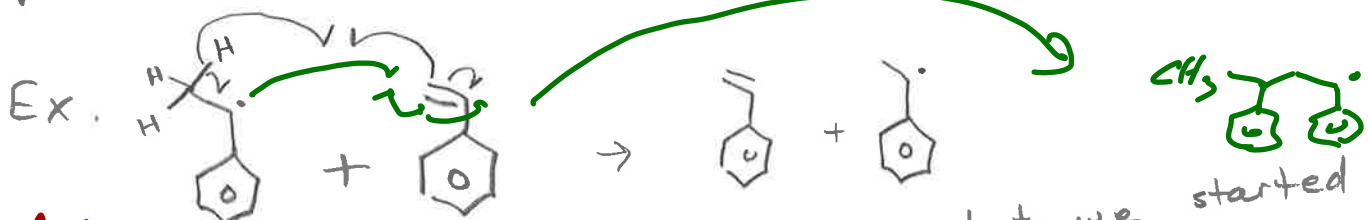


Agree - but because we generally want a better leaving group. Similar nature of the initiated monomer + this R group does not significantly favor K_{β}

I know that Z is a suitable choice, as the benzylic group is an effective EWG, which is necessary for an effective Z group. However, I do not believe R was the most optimal choice due to its stability as a 2° radical with benzene resonance stability.

(+1)

?? It is okay as a leaving group, but doesn't act as an optimal re-initiator as H abstraction may occur. *H would not serve as a leaving group*



*if this were to serve as a re-initiator **

This is what we started with.

