

Name: Zoe Guntov (Please write your name on each page)

79

Spring 2021 PSC 302 Exam 1 [Total: 100 pts] (Instructor: Patton)

During the exam, no notes, phones (or other electronic devices) or neighborly conversions 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. [2 pts] For a general free radical polymerization, what happens to the overall rate of polymerization at steady state if we double the concentration of monomer? (circle the correct answer)

- ✓ a) R_p does not depend on $[M]$ so nothing changes
 b) R_p doubles
 c) R_p increases by a factor $\sqrt{2}$
 d) R_p decreases by half

$$R_p = k_p [M][M^*]$$

2. [2 pts] Which is the rate determining step of radical chain initiation? (circle the correct answer)

- ✓ a) initiator decomposition
 b) chain initiation of monomer
 c) chain propagation
 d) none of the mentioned

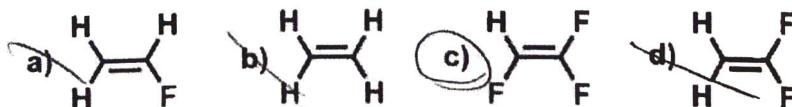
3. [2 pts] Which mode in the chain termination step is accompanied by a transfer of hydrogen atom? (circle the correct answer)

- ✓ a) combination
 b) disproportionation
 c) both combination and disproportionation
 d) none of the above

4. [2 pts] How does polymerization rate at a given monomer concentration vary, if rate of chain initiation is tripled? (circle the correct answer)

- ✓ a) doubled
 b) tripled
 c) increment by factor of $3^{0.5}$
 d) remains constant

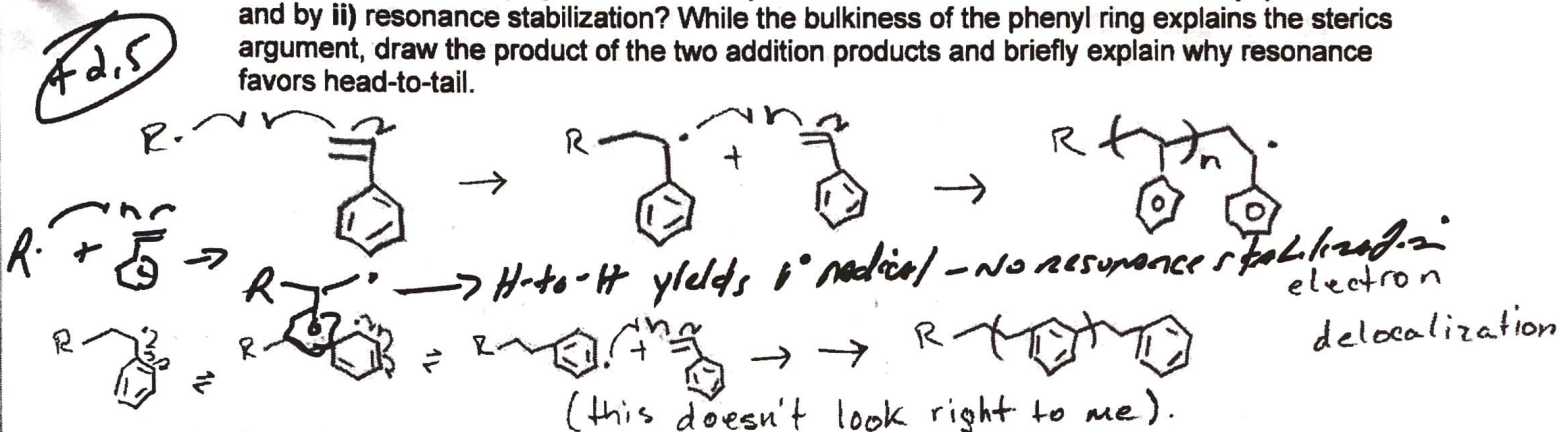
5. [2 pts] Ignoring regioselectivity, which of the following olefins is expected to have highest relative rate of addition by a methyl radical ($\bullet\text{CH}_3$)? (circle the correct answer)



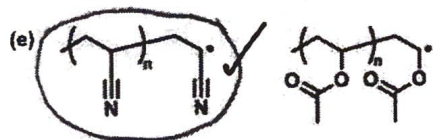
+10

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


6. [5 pts] In the radical polymerization of styrene, head-to-tail addition is favored by i) sterics and by ii) resonance stabilization? While the bulkiness of the phenyl ring explains the sterics argument, draw the product of the two addition products and briefly explain why resonance favors head-to-tail.



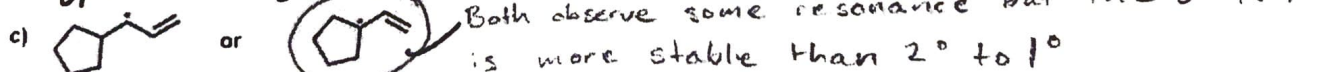
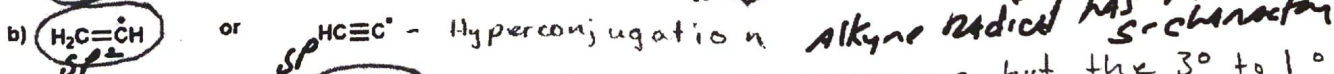
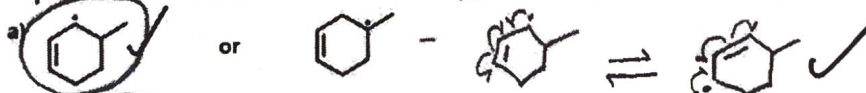
7. [5 pts] For each pair of radicals below, circle the radical with more electrophilic character.


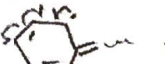



Ignore this ↓

~~I started to choose  because of the more e- O, but questions 5 & 12 make me think that inductive effects play a bigger role, making the very electrophilic C more appropriate.~~

8. [5 pts] Indicate which member of each pair represents the most stable radical and provide a brief explanation for your choice. If resonance is part of your explanation, please show all possible resonance structures. Resonance stabilized



+2.5 Though it is secondary compared to tertiary, resonance stabilized and outranks stability.  ⇌  ⇌  etc.

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

9. [20 pts] Given the sequence of reactions below for a radical polymerization, "derive" the overall kinetic rate expression (R_p) for a polymerization initiated by thermal homolysis of an initiator. Please identify all assumptions made to simplify the kinetic expression.



1. k_p is independent of DP ✓
2. Kinetic chain lengths are large ✓
3. Only 1 type of active site ✓
4. steady state approximation ✓
5. Long chain lengths, monomer is consumed in propagation, monomer consumption is negligible

$$R_t = R_i = 2k_t [M\cdot]^2 \rightarrow [M\cdot] = \left(\frac{R_i}{2k_t} \right)^{1/2}$$

and $R_i = R_d = 2fk_d [I]$ so, $[M\cdot] = \left(\frac{fk_d [I]}{k_t} \right)^{1/2}$

plug into $R_p = k_p [M] \times [M\cdot]$

since R_i is negligible, solve for R_p

$$R_p = k_p [M] \left(\frac{fk_d [I]}{k_t} \right)^{1/2} \checkmark$$

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

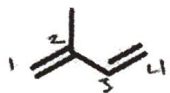
10. [10 pts] Geometric isomerism: Draw the mechanism and the resulting repeat units following

a) exclusively 1,2-addition

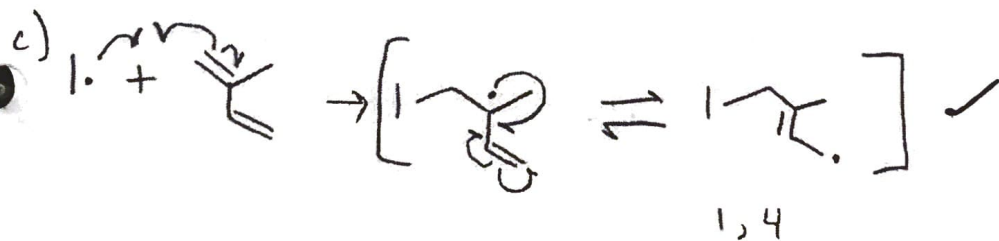
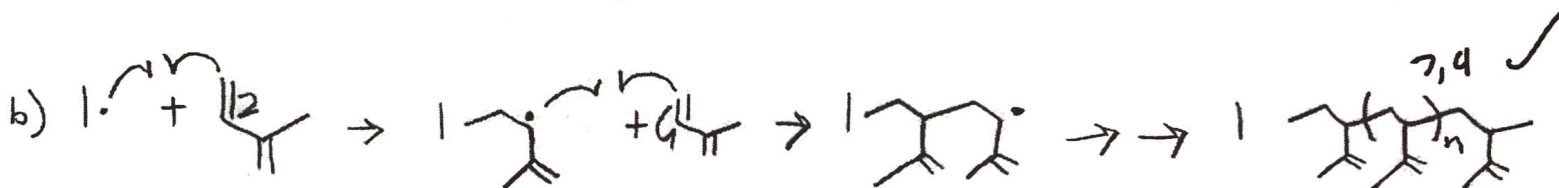
b) exclusively 3,4-addition

c) exclusively 1,4-addition

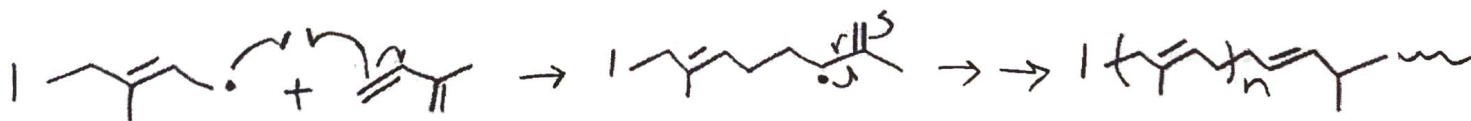
for radical polymerization of 1,3-isoprene. Use $I\cdot$ as a generic initiator. You will need to propagate the chain at least two monomer units to obtain the repeat units.



1,3-isoprene



Good

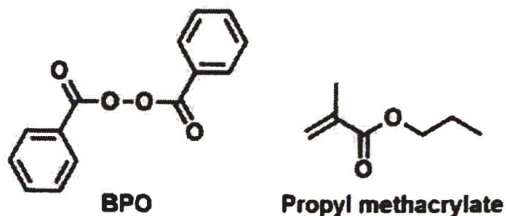


4 (+10)

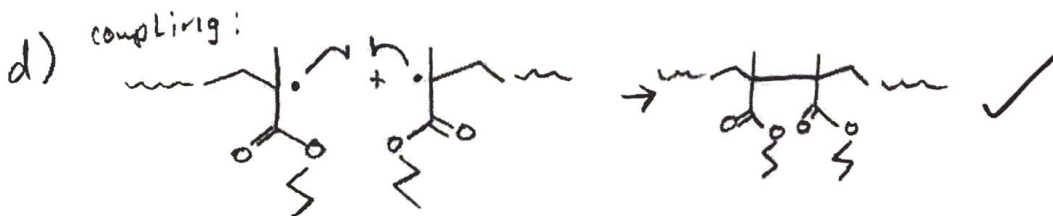
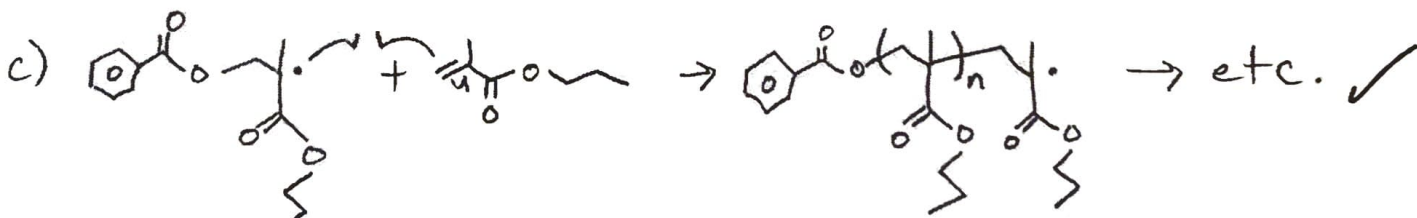
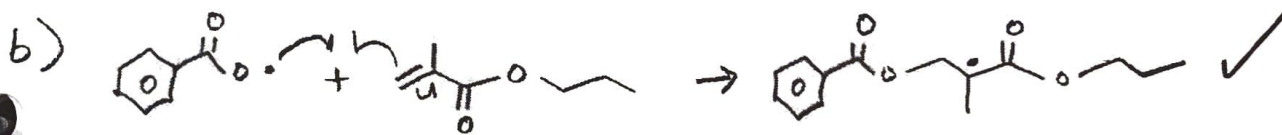
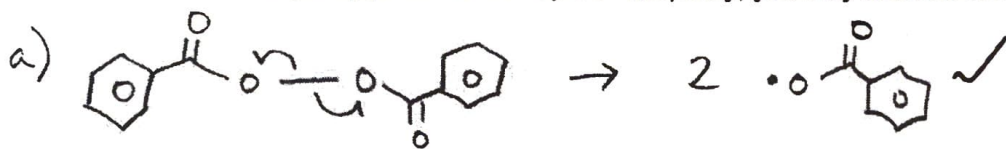
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11. [25 pts] Illustrate the mechanisms (be sure to push the arrows) for steps (a) – (d) during thermal polymerization of propyl methacrylate at 60 °C with benzoyl peroxide initiator as shown below. Then address the answer the (e).

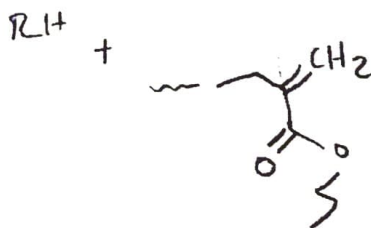
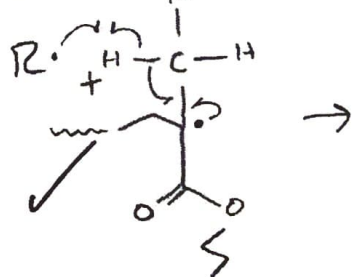
- Initiator decomposition
- Addition of primary radical to monomer
- Propagation
- Termination – both modes (coupling and disproportionation)



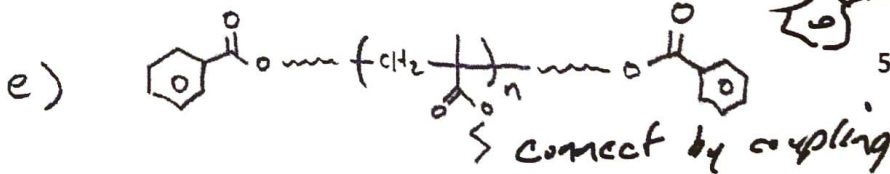
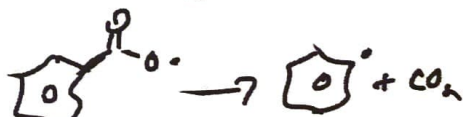
e) Show the possible polymer chain ends if the polymerization were carried out at 100 °C (as opposed to 60 °C). For simplicity, you may assume termination by coupling.



disproportionation:



At high temps



+23

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

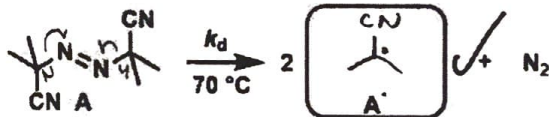
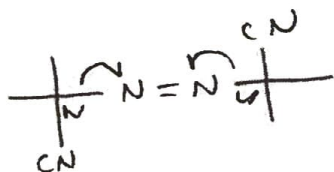
12. (20 pts) Entropic Doom, Inc. – a contract polymer synthesis startup company experienced a decrease in the rate of monomer initiation when changing from their original initiator A to a new initiator B ($R_{i,A} > R_{i,B}$) for the industrial polymerization of acrylonitrile at 70 °C. Assume the rate constant for initiator decomposition is approximately equal for the two initiators, so $k_{d,A} \approx k_{d,B}$. Also assume the concentration, initiator efficiency (f), and half-lives of both initiators are approximately equal under these reaction conditions.

i) Show the mechanism for the thermal decomposition of both azo initiators and provide the structure of each radical A· to B· formed in the boxes provided (driving force for decomposition of each initiator is the release of nitrogen gas).

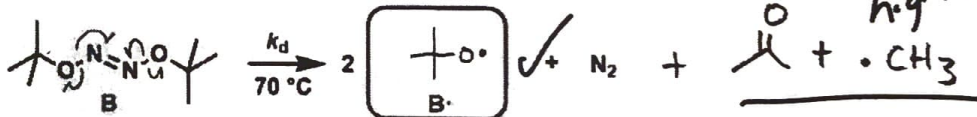
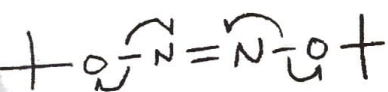
ii) Provide the company with a detailed explanation for the observed decrease in initiation rate for acrylonitrile when using initiator B. Use arguments based on sterics, polarity, etc. as appropriate.



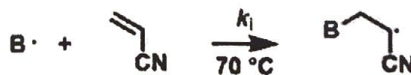
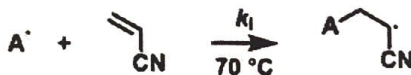
i) Initiator decomposition step (assume k_d for A \approx k_d for B)



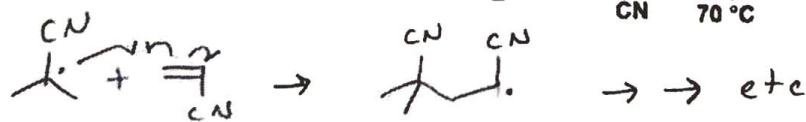
yes, but mostly higher temp



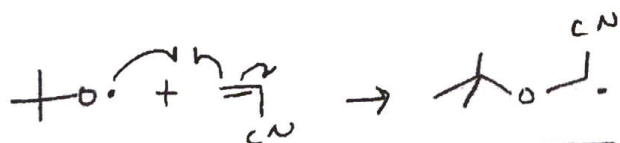
ii) Monomer initiation step (observed $k_{i,A} > k_{i,B}$)



This answer to ii) is driven primarily by polarity



$\overline{\text{CN}} \Rightarrow e^-$ deficient alkene



A· is more nucleophilic than would show a higher rate of initiation than the electrophilic B·

Though O· is the more electronegative atom, it forms a secondary product that slows down initiation. The EWG, nitrile succeeds in this case since no secondary products can form.

(+12)