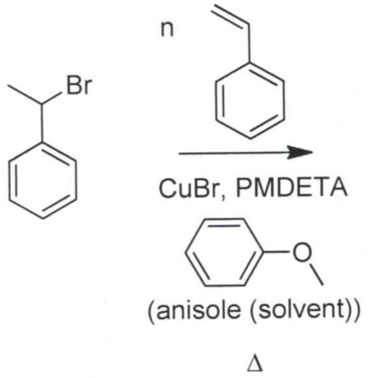
Name: ANSWER KEY [printed]

"On my honor, as an Aggie, I have neither given nor received unauthorized aid on this academic work."

________________________[signature]

Exam IV, April 21, 2011, 125 pts
Polymer Chemistry, CHEM 466, Spring 2011
Texas A&M University, College Station, TX, USA

1. For the following atom transfer radical polymerization of styrene in anisole, initiated by α-bromoethylbenzene, and using CuBr and *N,N,N',N",N"*-pentamethyldiethylenetriamine (PMDETA) as the catalyst/ligand system:



$n = 80$

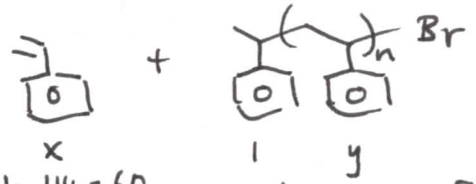
(a) Give the full structure for the polymer product (draw above). **[10 points]**

(b) Calculate the initiator efficiency, given that the initial monomer concentration is 0.1 mol/L, the initial concentrations of α-bromoethylbenzene and CuBr are 0.001 mol/L each (with an excess of PMDETA ligand), and ^{1}H NMR data indicate an integration value of 500 for the 5 overlapping phenyl protons of the initiator, monomer and polymer repeat units (anisole removed), and an integration value of 60 for the ~~for the~~ combined 3 vinylic protons of the unreacted monomer. **[10 points]**

$$DP_n = \frac{[M]_0 \cdot \%\text{ monomer conv.}}{[I]_0 \cdot f}$$

$$80 = \frac{0.1\ \text{mol/L} \cdot 0.8}{0.001\ \text{mol/L} \cdot f}$$

$$\Rightarrow \boxed{f = 1.0}$$



3 vinylic ^{1}H's = 60 $\Rightarrow x = 20$

5 Ar ^{1}H's = 500 $\Rightarrow x + 1 + y = 100$

$\Rightarrow y = 100 - 20 - 1 = 79 = 80$ (w/ 1 sig figs)

$\Rightarrow$ % M conv. = 80%

and $DP_n = 80$ (w/ 1 sig figs)

(c) Insert the calculated value for the degree of polymerization onto your structure for part (a). **[5 points]**

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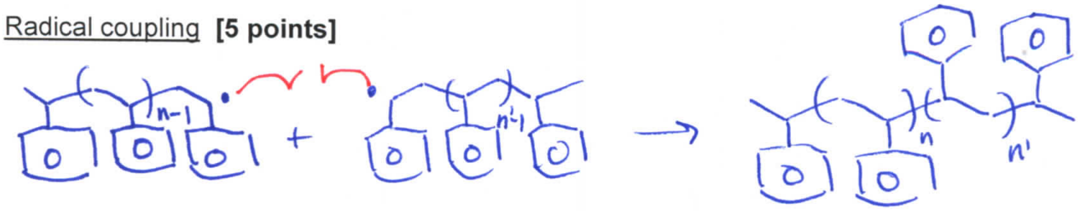
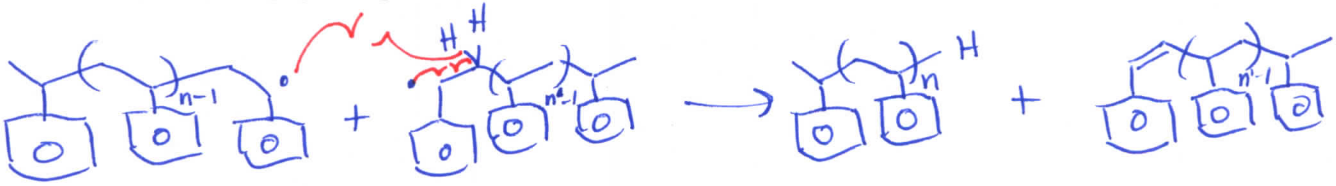
(d) Draw the electron arrow-pushing mechanisms and give the polymer products that would occur from terminations by radical coupling and disproportionation.

Radical coupling **[5 points]**



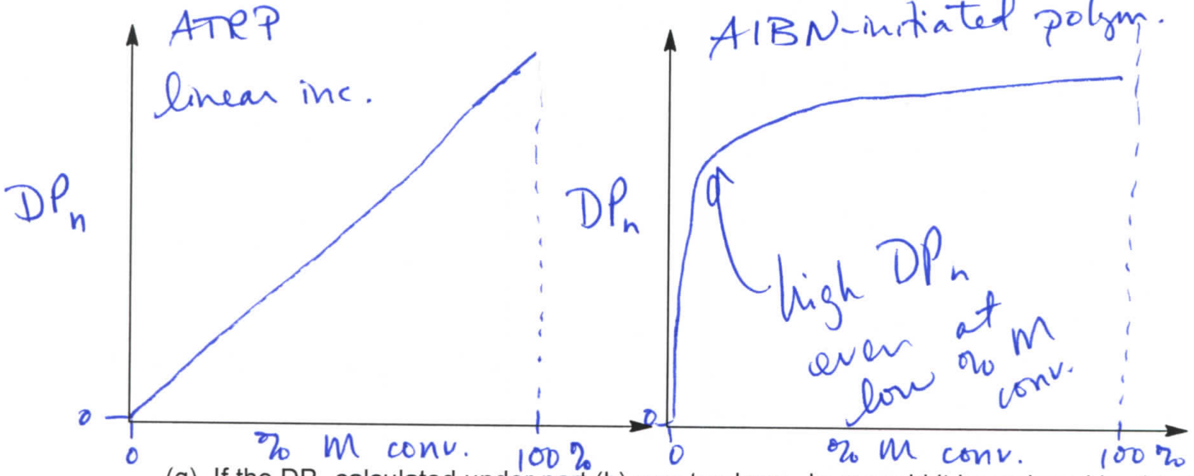
Disproportionation **[5 points]**



(e) Why are irreversible termination and chain transfer reactions limited for this polymerization of styrene, in comparison to polymerization of styrene initiated by azobisisobutyronitrile (AIBN)? **[5 points]**

reversible termination rxns limit the radical concentration

(f) On the axes below, draw the growth profiles of DP_n *vs.* % monomer conversion that would be expected for this controlled ATRP of styrene and traditional styrene polymerization using AIBN (don't forget to label the axes and your plots). **[5 points]**



(g) If the DP_n calculated under part (b) was too large, how could it be reduced by this ATRP method? **[5 points]**

quench the polym. at an earlier time pt., at lower % monomer conversion

(h) How could the DP_n be reduced during the traditional AIBN-initiated polymerization? **[5 points]**

use a chain transfer agent

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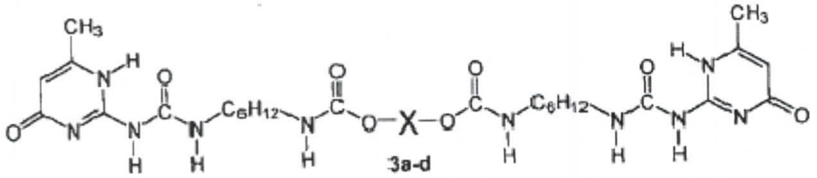
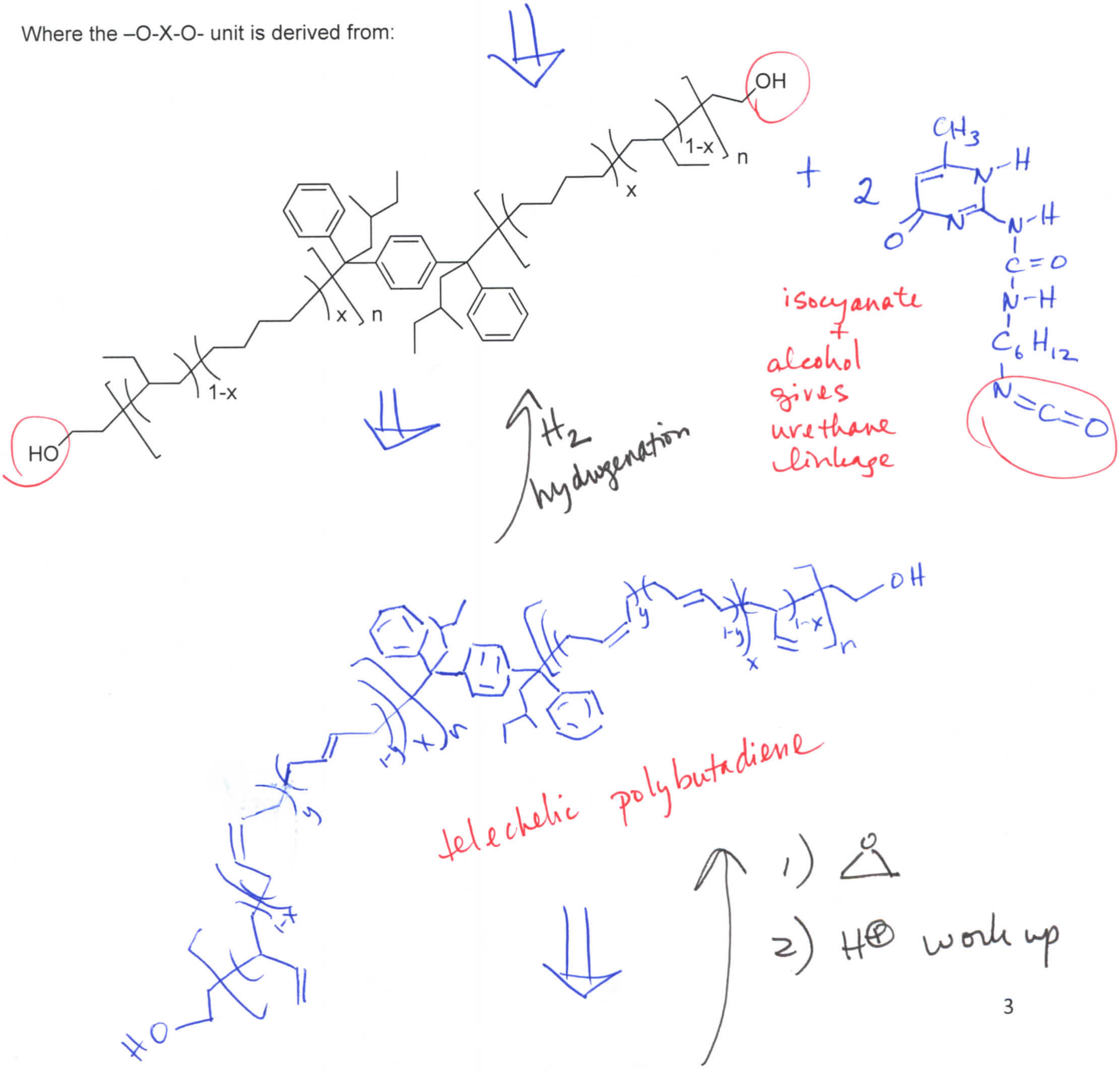
2. During our first class lecture, we discussed supramolecular polymer materials as described in Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; van der Rijt, J. A. J.; Meijer, E. W. *Adv. Mater.* **2000**, *12*(12), 874-878, and you were told that, by the end of the semester, you would be able to propose synthetic routes to produce each of the supramolecular polymer systems reported. Provide a retrosynthetic approach to the following structure, **3**. A few hints: Work backwards from the final structure (3, given below); look for parts of **3** and the exact polymer structure (-O-X-O-) that you recognize; hydrogenation of an initially prepared analog of the HO-X-OH polymer is involved. **[20 points]**



Where the –O-X-O- unit is derived from:



isocyanate + alcohol gives urethane linkage

H2 hydrogenation

telechelic polybutadiene

1) [epoxide]

2) H⊕ work up

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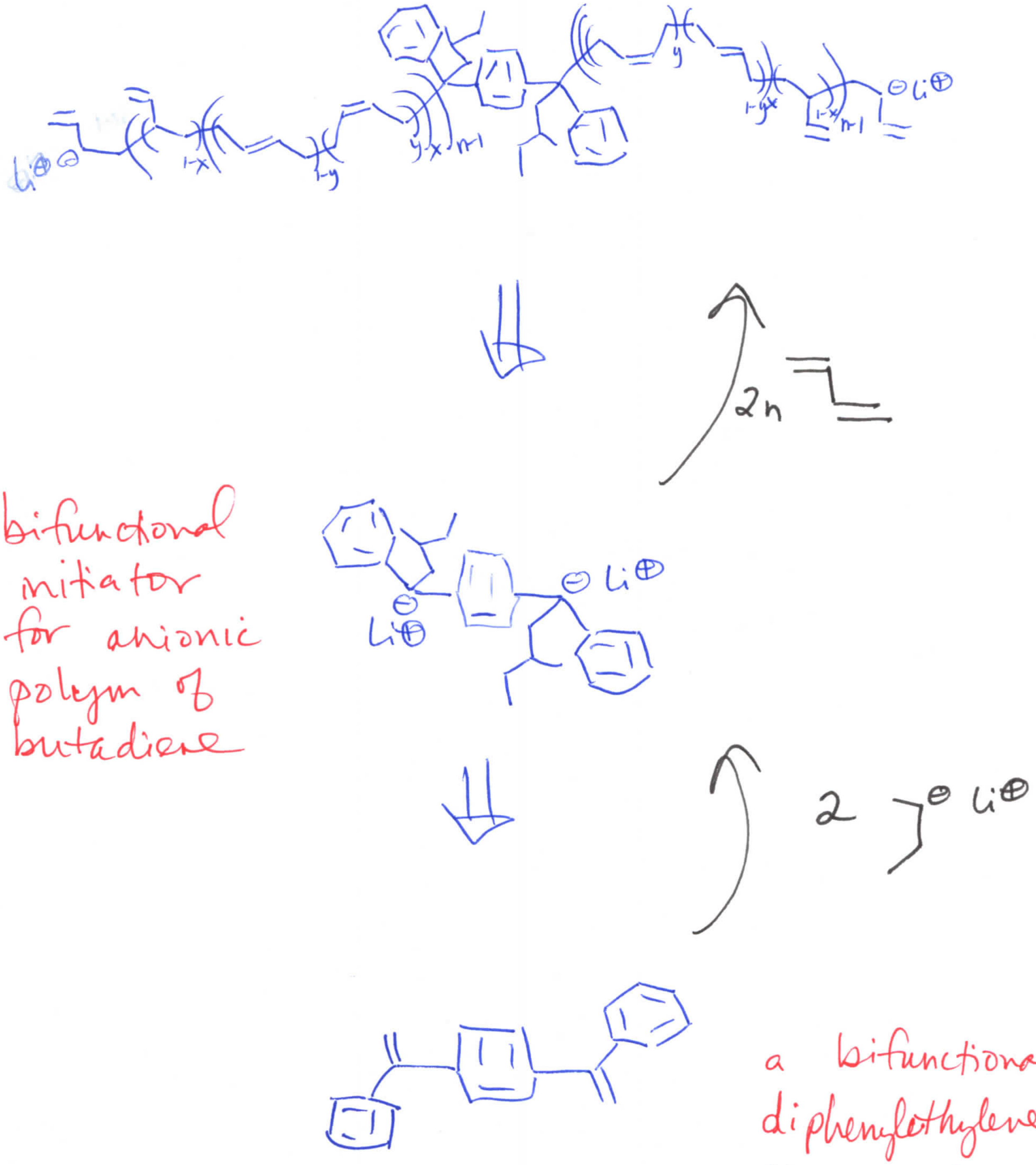
2. (con't.) rxn w/ $\overset{O}{\triangle}$ adds one unit to each end; ethylene oxide does not propagate w/ $Li^{\oplus}$ counterion



bifunctional initiator for anionic polym of butadiene

a bifunctional diphenylethylene allows for pre-formation of a bifunctional initiator

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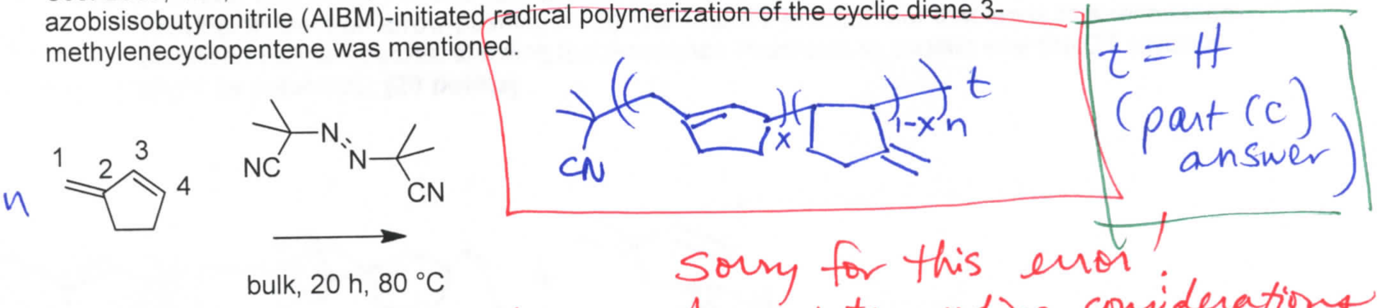
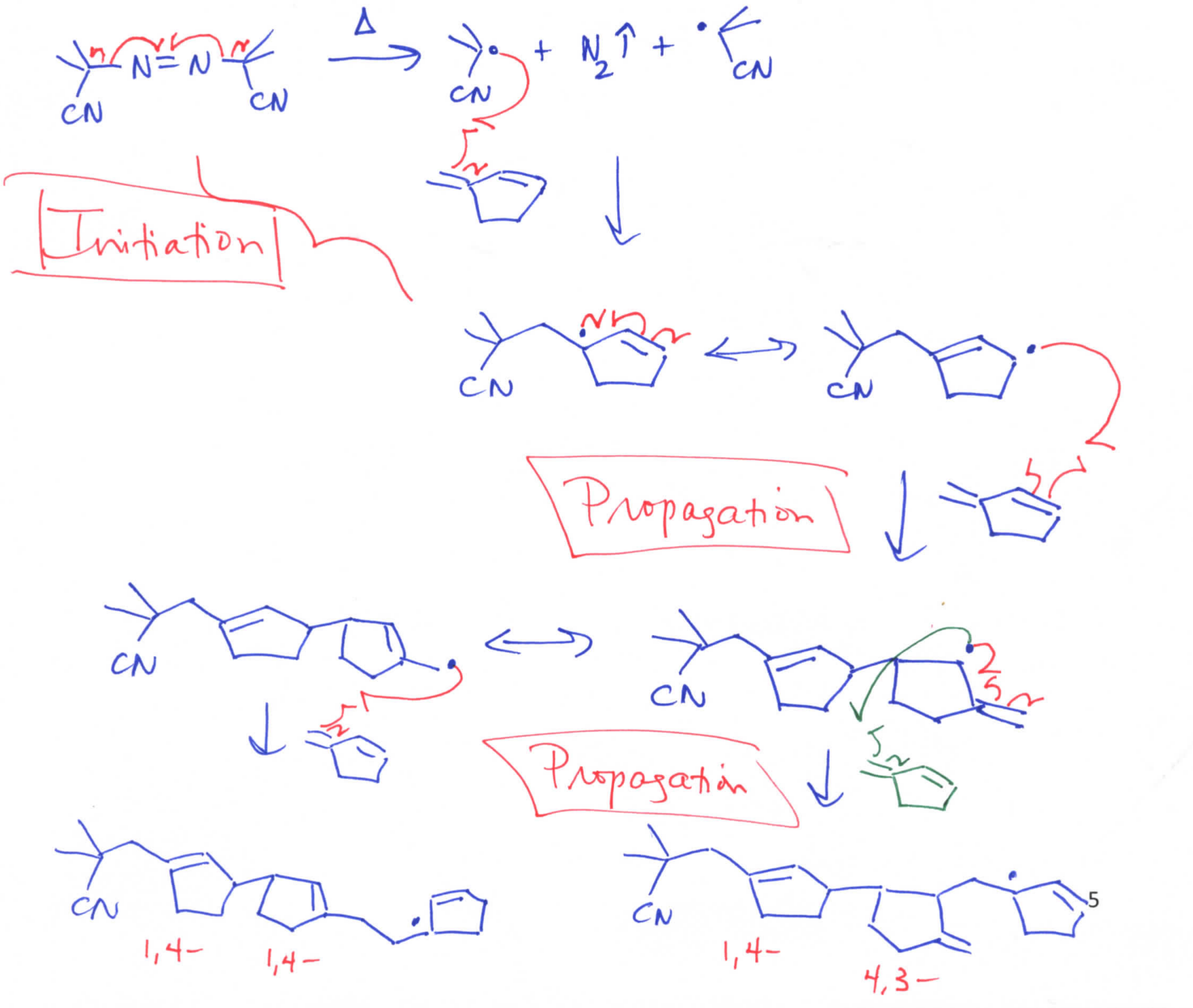
3. During our discussion of the article Kobayashi, S.; Lu, C.; Hoye, T. R.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2009**, *131*, 7960-7961, the limited degree of polymerization (DP_n ~ 10) obtained by traditional azobisisobutyronitrile (AIBM)-initiated radical polymerization of the cyclic diene 3-methylenecyclopentene was mentioned.



Sorry for this error! Appropriate grading considerations have been made.

(a) Provide the electron arrow-pushing mechanistic steps for **initiation** and **propagation** to give the polymer having ~~1,2-~~ 4,3- and 1,4-regiochemistries (please note, the numbering for the nomenclature of the monomer (3-methylenecyclopentene) is opposite to the numbering of the monomer diene and the resulting repeat units), label the steps, show resonance structures, and show the chemical structure for the polymer. **[20 points]**



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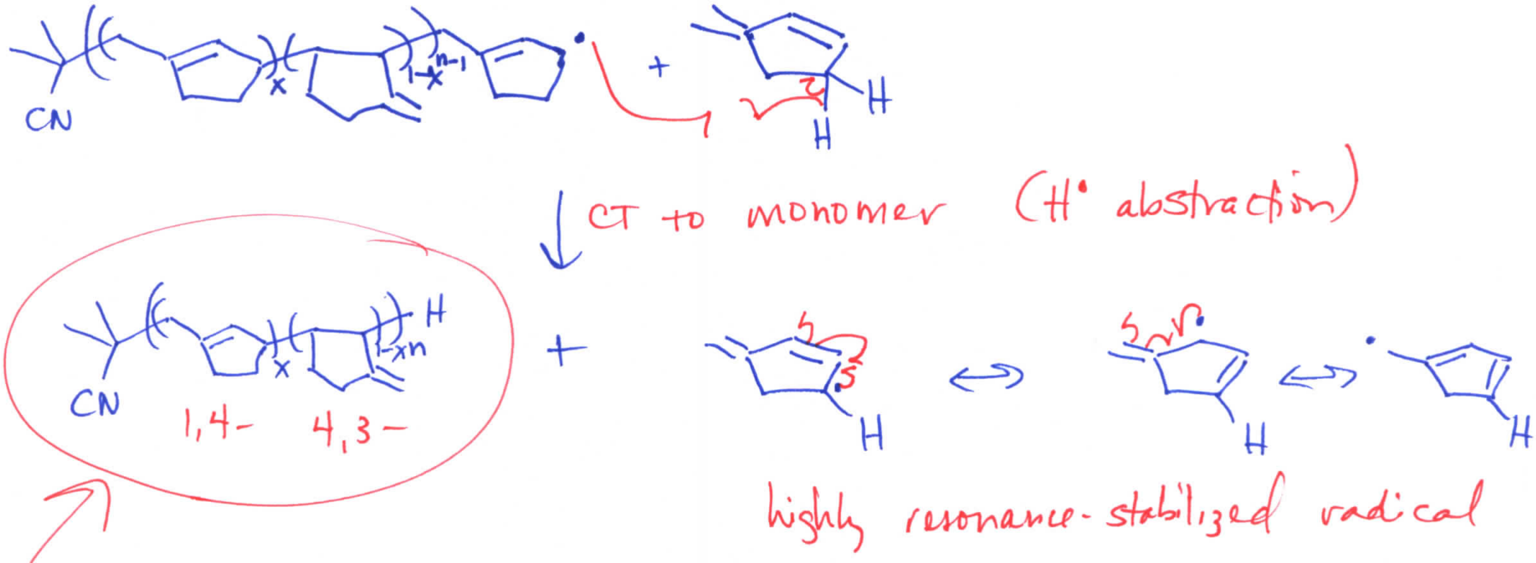
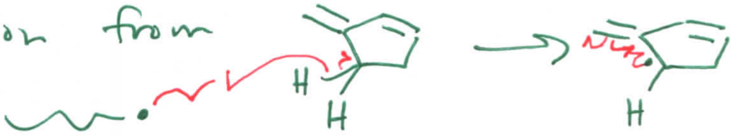
(b) It is likely that chain-transfer (CT) reactions to monomer are responsible for the limited DP_n. Provide an electron arrow-pushing mechanism for CT to monomer that leads to a resonance-stabilized radical species, showing the resonance structures to explain why the CT reaction might be prevalent. **[20 points]**

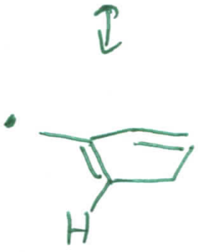


highly resonance-stabilized radical

alternatively, H• abstraction from



given also an allylic, resonance-stabilized radical although less conjugated than the one above



(c) Given the stated prevalence of CT to monomer, include the appropriate chain end on your structure for part (a). **[5 points]** t = H and also shown

(d) Do you predict that this monomer has a relatively high or low chain transfer constant? **[5 points]**

a high CT constant is predicted, and confirmed by the limited DP_n obtainable

Equations, which may be of use:

Number-average molecular weight:

$$M_n = \frac{\Sigma N_x M_x}{\Sigma N_x}$$

$$N_x = \#\text{ moles of polymer chains having molecular weight, } M_x$$

Weight-average molecular weight:

$$M_w = \Sigma w_x M_x = \frac{\Sigma N_x M_x^2}{\Sigma N_x M_x}$$

$$w_x = \text{wt fraction of polymer chains having molecular weight, } M_x = \frac{N_x M_x}{\Sigma N_x M_x}$$

Degree of polymerization:

$$DP_n = \frac{1}{1 - c}$$

$$c = \text{extent of conversion of functional groups}$$

$$DP_n = \frac{[\text{monomer}]_0 \cdot \%\text{ monomer conversion}}{[\text{initiator}]_0 \cdot f}$$

Polydispersity index:

$$PDI = \frac{M_w}{M_n}$$

Critical extent of reaction:

$$p_c = \frac{2}{f_{av}}$$

Average degree of monomer functionality:

$$f_{av} = \frac{\Sigma N_i f_i}{\Sigma N_i}$$

Textbook:
Hiemenz, P. C.; Lodge, T. P. *Polymer Chemistry*, 2nd Edition; CRC Press, Taylor & Francis Group: Boca Raton, FL, USA, 2007