

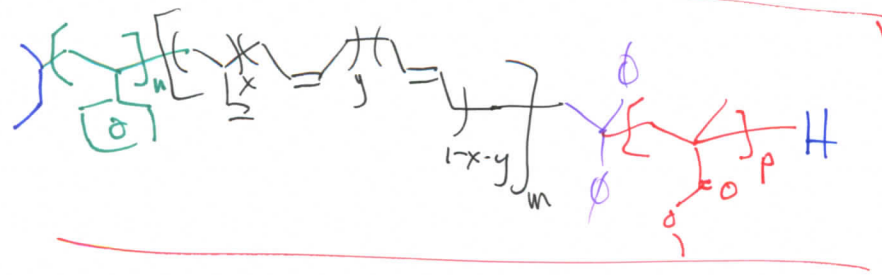
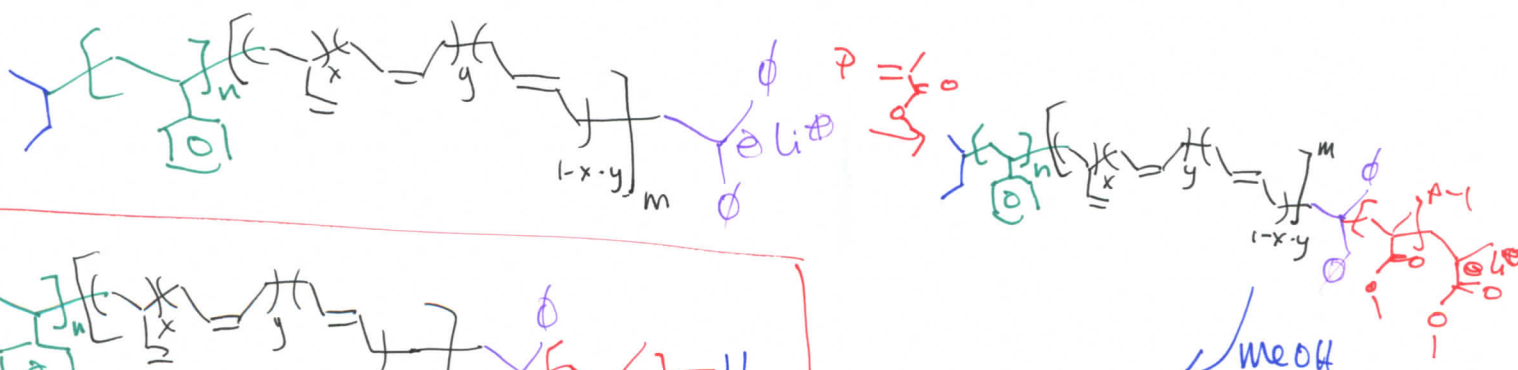
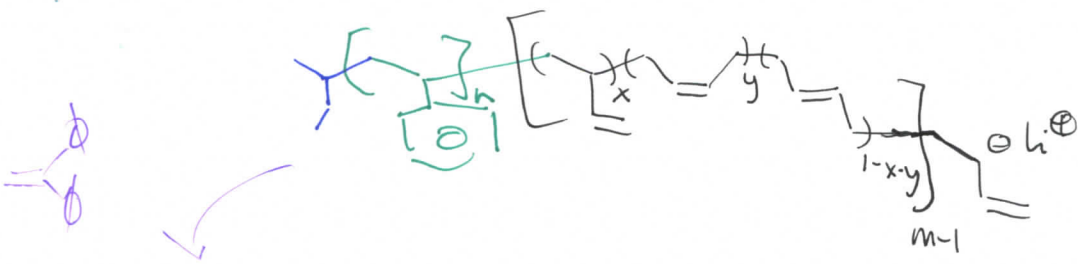
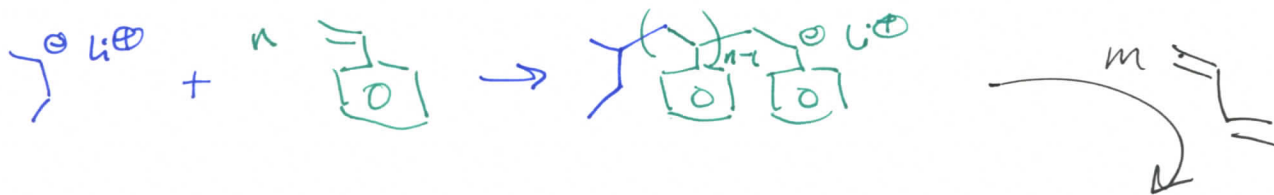
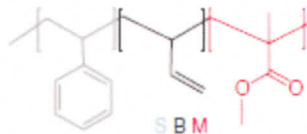
Name: ANSWER KEY [printed]

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

_____ [signature]

Exam IV, April 24, 2012, 100 pts
 Polymer Chemistry, CHEM 466, Spring 2012
 Texas A&M University, College Station, TX, USA

1. (a) Provide a sequence of reactions that could be followed as a forward synthetic approach to prepare a polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate) triblock copolymer (PS_n-*b*-PB_m-*b*-PMMA_p) via anionic polymerizations, showing the product(s) formed at each step. This type of triblock copolymer was drawn in abbreviated form (as reproduced below) in the publication, Gröschel, A. H.; Schacher, F. H.; Schmalz, H.; Borisov, O. V.; Zhulina, E. B.; Walther, A.; Müller, A. H. E. *Nature Communications* **2012**, 3:710, DOI: 10.1038/ncomms1707, and it was shown to undergo assembly into multicompartment micellar nanostructures. Based on your forward synthetic route, draw the exact chemical structure of the polymer, being certain to illustrate the chain ends, any potential regiochemical and stereochemical variations, additives required, etc. [10 points]



complete final structure

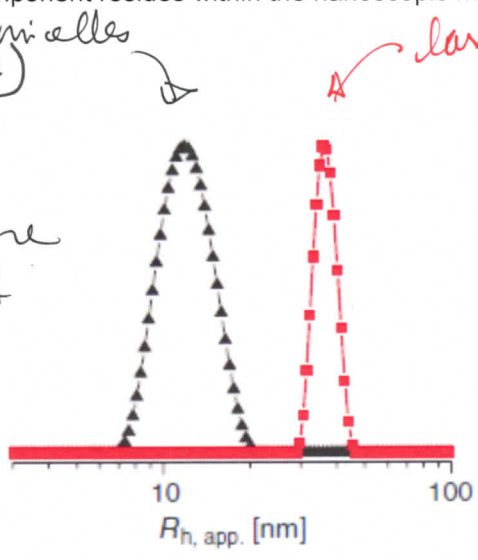
MeOH
1

(b) The supramolecularly-assembled multicompartment nanostructure morphologies and dimensions were found to be dependent on the block copolymer chain lengths and the solvent systems employed. For instance, when $PS_{337}\text{-}b\text{-}PB_{333}\text{-}b\text{-}PMMA_{369}$ was transitioned from *N,N*-dimethylacetamide (solvent for PS and PMMA, non-solvent for PB) to acetone/isopropanol mixtures (solvent for PMMA, non-solvent for PS and PB), 'clover' multicompartment micelles were produced. Explain the following dynamic light scattering data (each of the 2 plots) and transmission electron microscopy image (full scale bar = 200 nm, inset scale bar = 50 nm; staining was achieved with OsO_4), in terms of:

- (i) at which stage of the process they were acquired (*i.e.* with which solvent system) [3 points]
- (ii) what type(s) of morphology(ies) are present, and [3 points]
- (iii) where each polymer component resides within the nanoscopic morphology. [3 points]

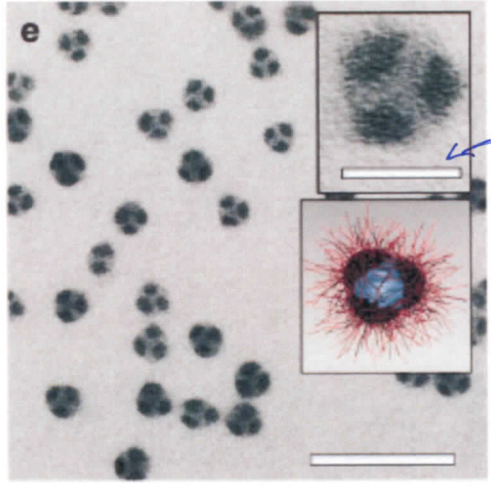
smaller size initial micelles
(called subunits in the article)

- (i) *N,N*-dimethylacetamide
- (ii) core-shell micelles
- (iii) PB collapsed in the core w/a shell of PS & PMMA



larger size from further assembly:

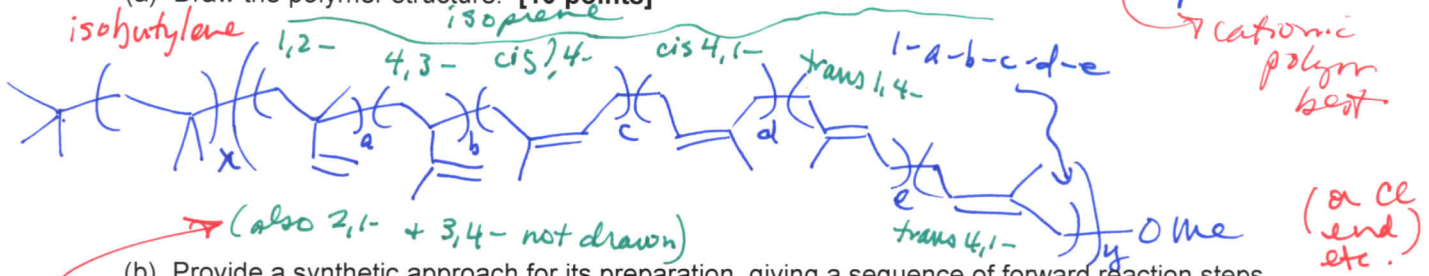
- (i) acetone/isopropanol mixture
- (ii) 'clover' multi-compartment micelles
- (iii) PB + PS compartments and PMMA corona



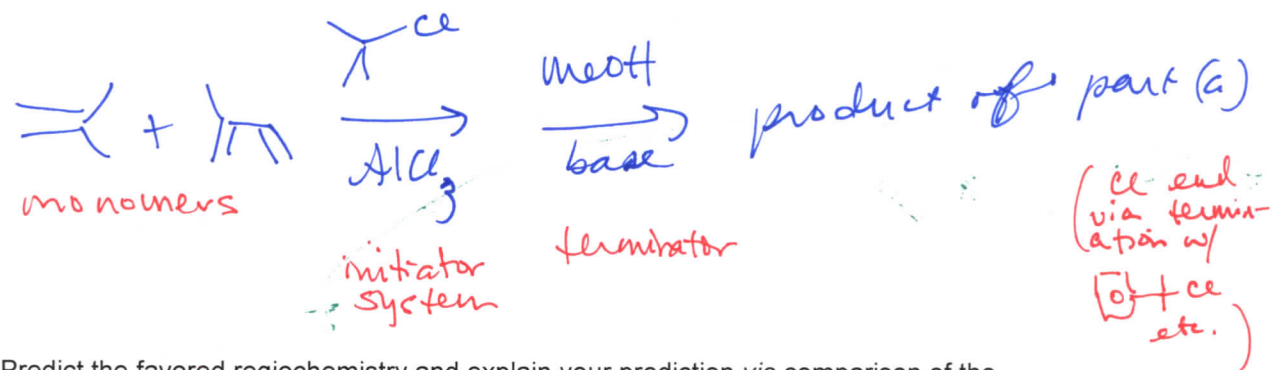
from 50-nm scale bar, ca. same size as observed by DLS

(i) } same as
(ii) } red DLS
(iii) } above

2. For the butyl rubber tubing located on the table in the front of the classroom:
 (a) Draw the polymer structure. [10 points]



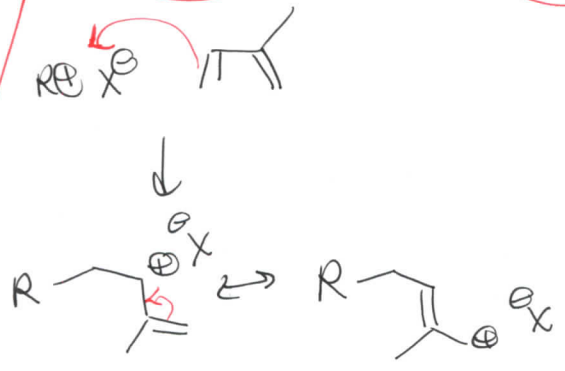
(b) Provide a synthetic approach for its preparation, giving a sequence of forward reaction steps that include your choices for initiator(s), monomer(s) and terminator(s), based upon your chemical structure of part (a). [5 points] many possible answers, depend on (a)



(c) Predict the favored regiochemistry and explain your prediction via comparison of the intermediates that lead to the possible repeat unit regiochemistries. [10 points]

both are highly improbable b/c carbocation intermediate would not be allylic + would be 1°
 e.g. for 2,1-

1,2- is favored b/c of 3° allylic carbocation intermediate



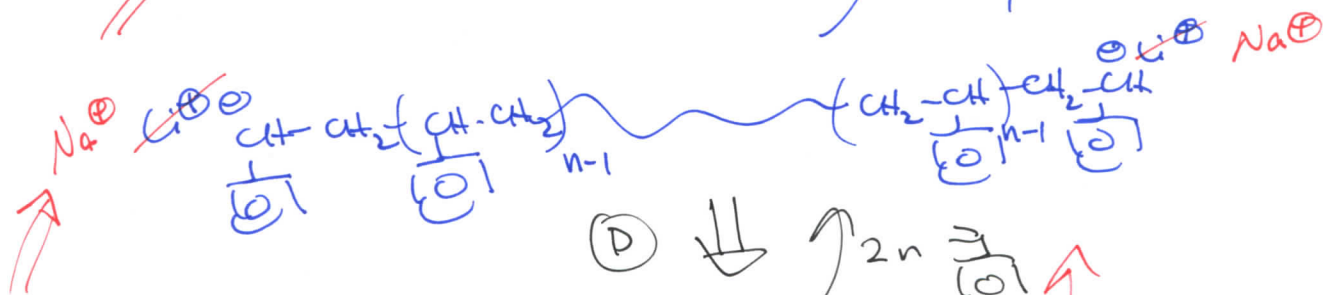
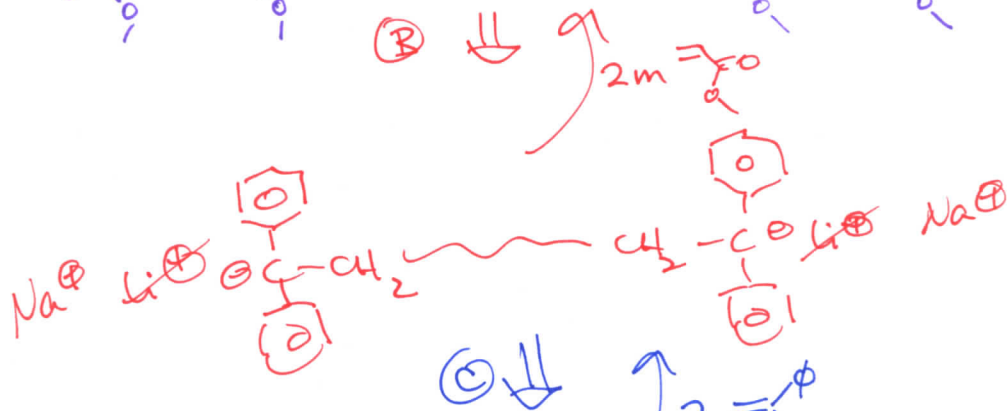
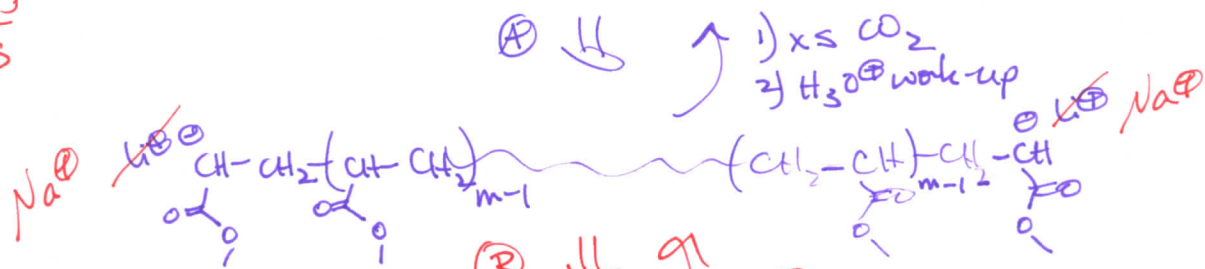
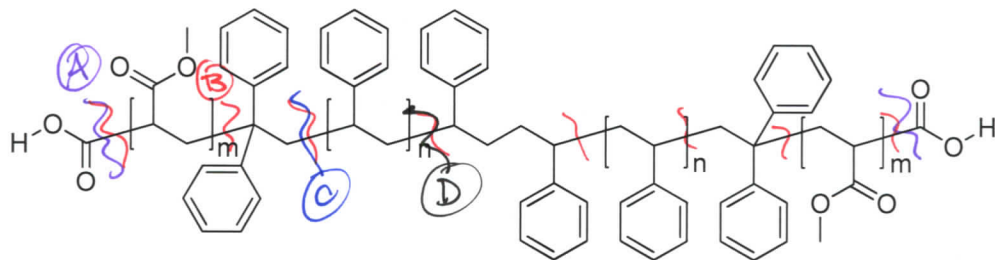
allylic w/ 2° + 1° carbocationic centers

cis 1,4- and trans 1,4- are also favored as they originate from the same intermediate

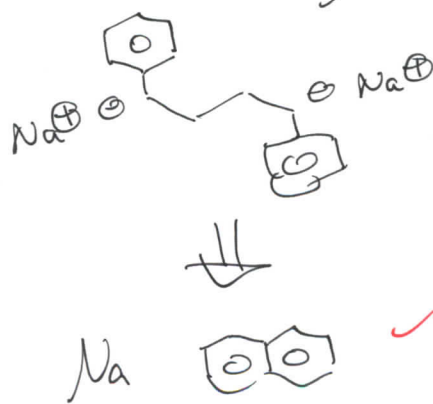
3. Provide retrosyntheses for the following poly(methyl acrylate)-*b*-polystyrene-*b*-poly(methyl acrylate) structures.

(a) [10 points]

① recognize different segments + the symmetry, then work backwards



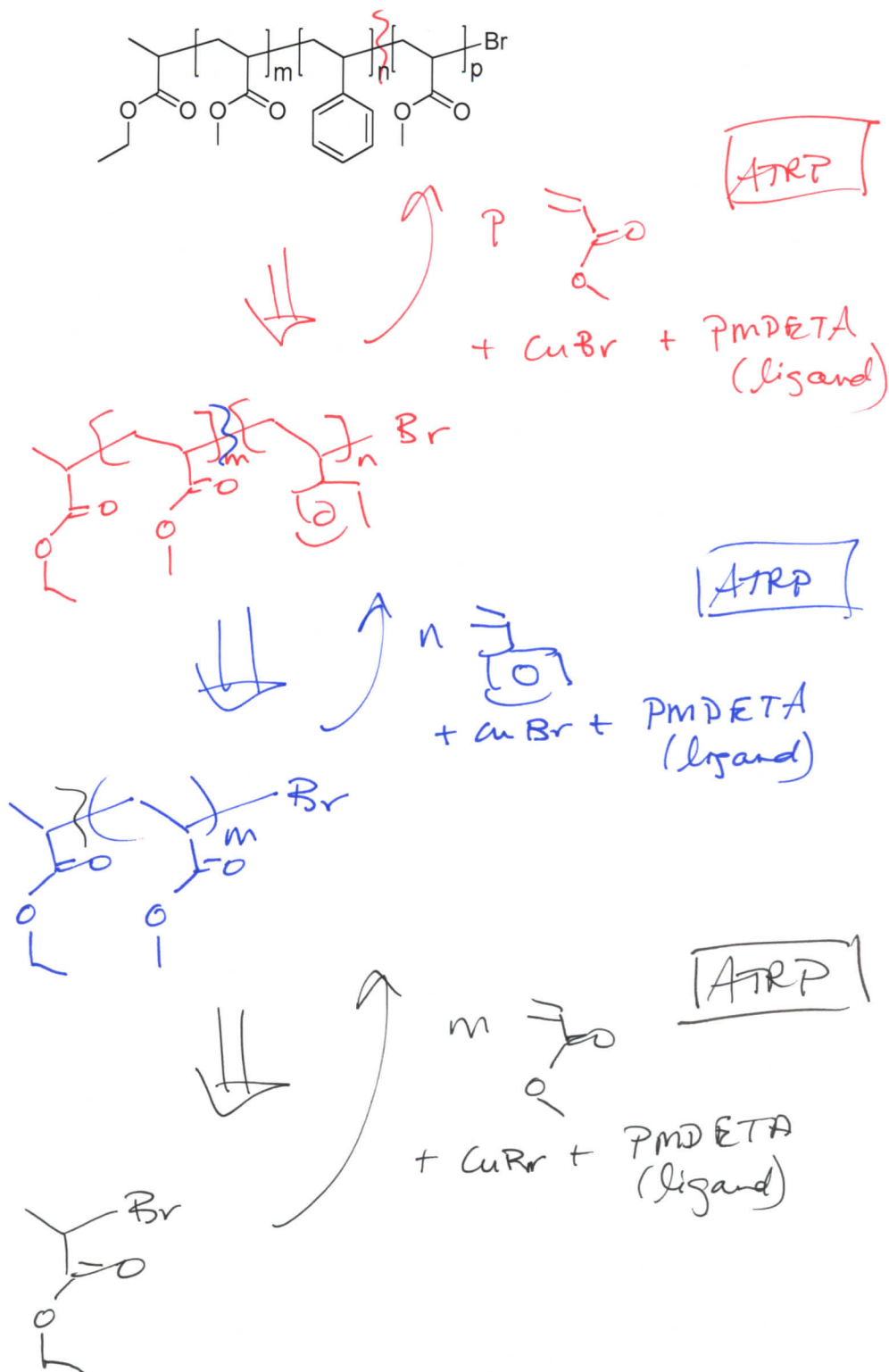
④ At this pt., the need for Na^+ as the counterion is recognized to produce the bifunctional initiator ...



... with the overall step multump

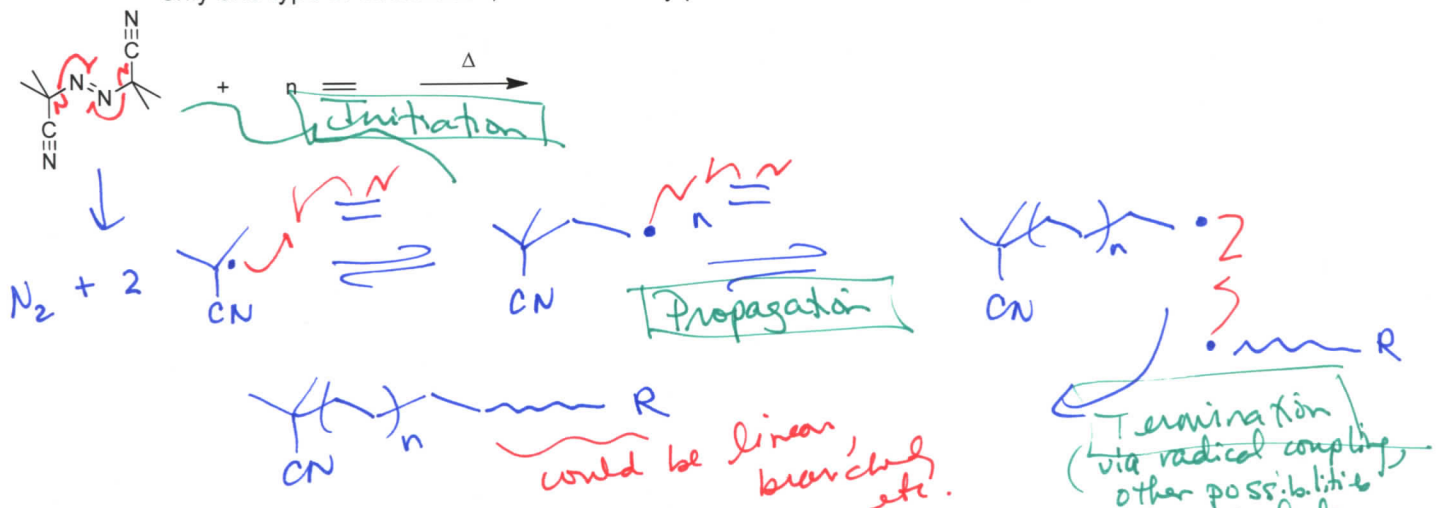


(b) [6 points]



4. For the low-density polyethylene (LDPE) packing material located on the table at the front of the classroom:

(a) Draw the electron arrow-pushing mechanism for the azobisisobutyronitrile-initiated radical polymerization of ethylene, and label each of the initiation, propagation and termination (show only one type of termination, from the many possible reactions discussed) steps. [10 points]

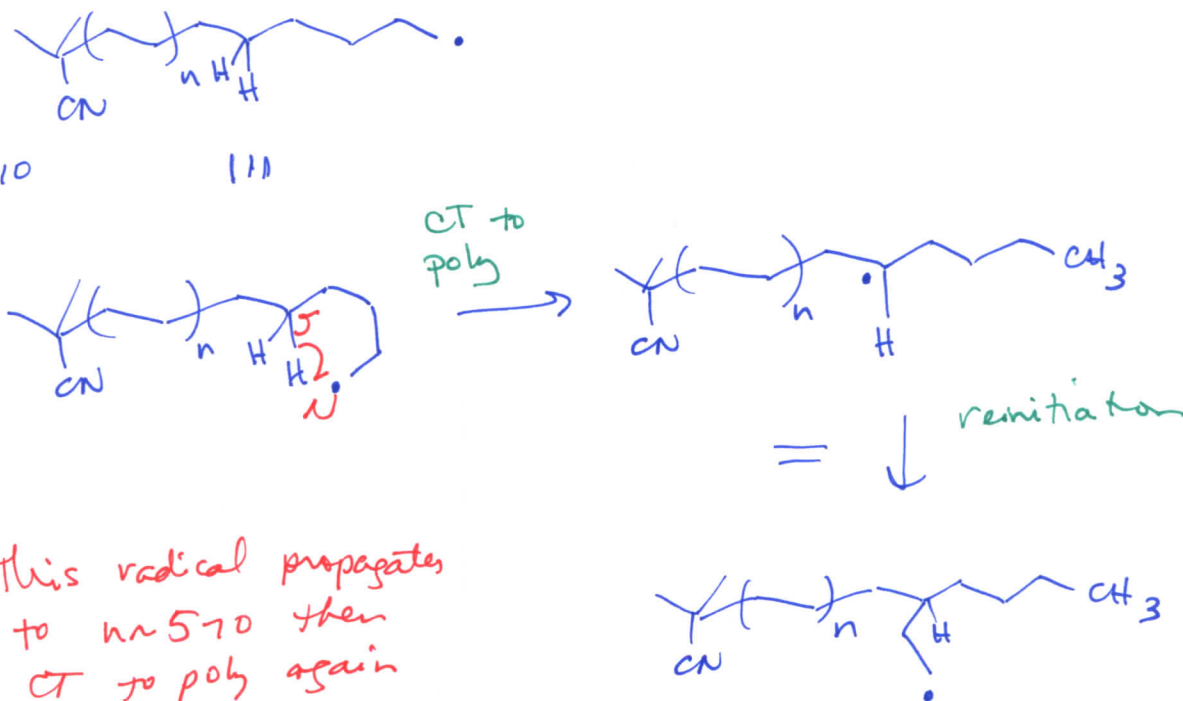


(b) What is the predominant termination reaction that occurs and leads to the low density of LDPE? [2 points]

backbiting chain transfer to polymer

include
disproportionation
chain transfer
rxns, ...

(c) Provide an electron arrow-pushing mechanism for your answer to (b). [8 points]



This radical propagates to n ~ 5-10 then CT to poly again followed by repetition of these steps many times

5. During the anionic vs. cationic polymerization of the cyclic diene monomer, **2**, as reported by Kobayashi, S.; Lu, C.; Hoyer, T. R.; and Hillmyer, M. A. *J. Am. Chem. Soc.* **2009**, *131*, 7960-7961:

(a) Explain the conclusions that can be drawn from the ^1H NMR data of Figure 1, regarding the repeat unit regiochemical outcomes, as a function of the reaction conditions and the type of polymerization chemistry. [10 points]

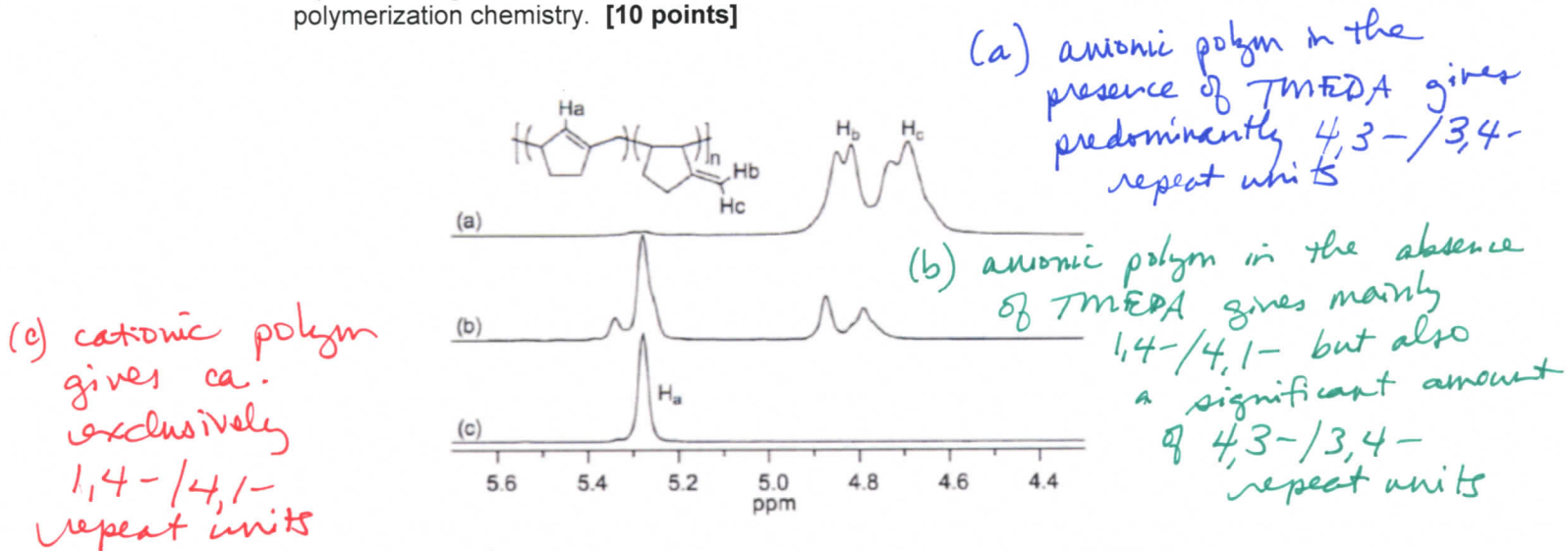
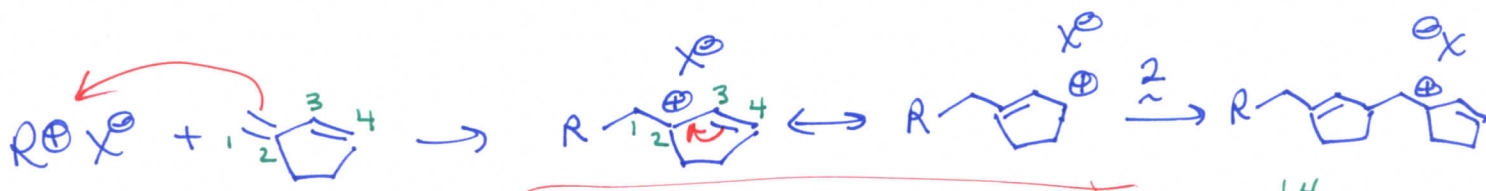
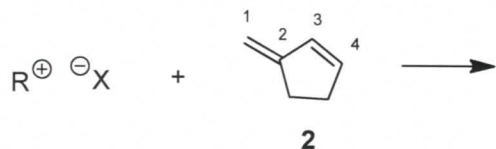


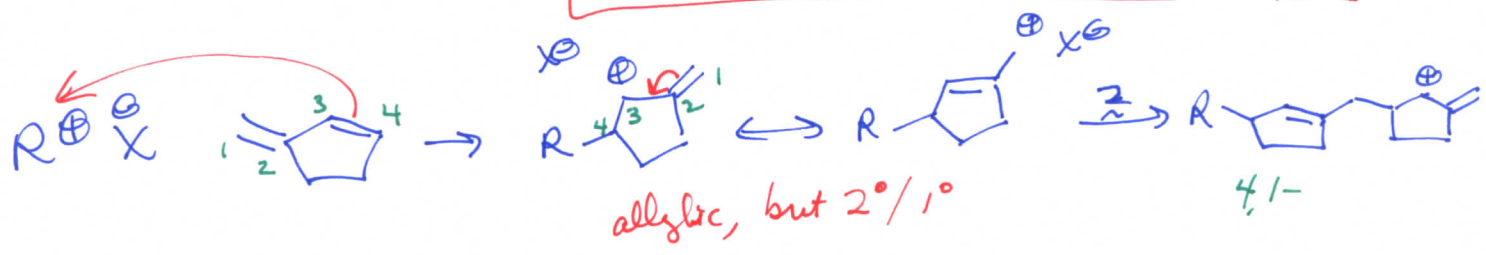
Figure 1. ^1H NMR spectra of poly-2 prepared with (a) *s*-BuLi/TMEDA, (b) *s*-BuLi, and (c) *i*-BuOCH(Cl)Me/ZnCl₂/Et₂O.

- (b) For the cationic polymerization conditions, use the general $R^+ X^- + \text{monomer } 2$ reaction below, (redrawing it repeatedly, as many times as necessary), to show the electron arrow-pushing mechanism for addition reactions, giving all possible regiochemistries for the carbocation intermediates that could result. Compare their relative stabilities to explain the ca. 100% regiochemical control (i.e. explain why only one regioisomeric repeat unit was observed, and which one it is). [10 points]



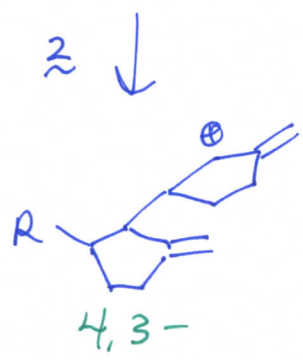
allylic $3^\circ/2^\circ$ carbocationic species highly stable (relative to others)

\therefore exclusively 1,4-regiochem for repeat units



allylic, but $2^\circ/1^\circ$

4,1-



4,3-