Name: ANSWER KEY [printed]

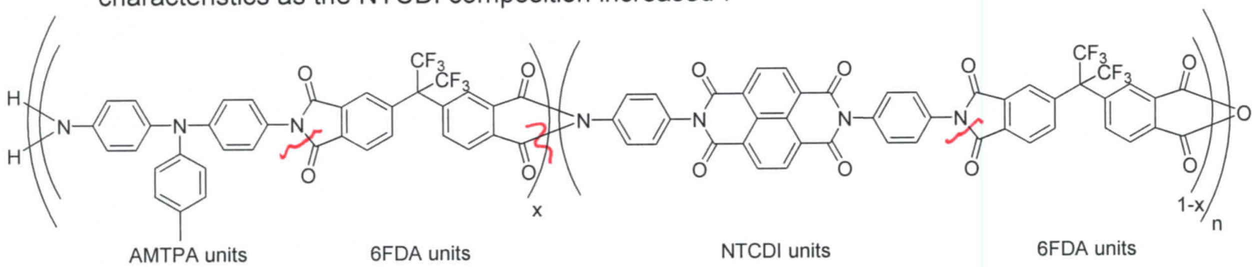
"On my honor, as an Aggie, I have neither given nor received unauthorized aid on this academic work."

_______________________ [signature]

Final Exam, May 3, 2013, 100 pts
Polymer Chemistry, CHEM 466, Spring 2013
Texas A&M University, College Station, TX, USA

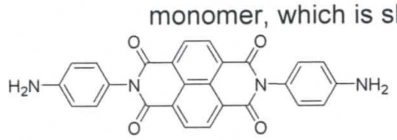
(*) the authors employed [structure] + [structure] to facilitate imidation

1. The copolyimide shown below was reported recently[1] to exhibit tunable optical and electronic properties through charge transfer between the AMTPA and NTCDI units. Memory devices constructed from a series of these copolymers, with variation in the x value, gave a change from "volatile dynamic random access memory to nonvolatile write once read many memory characteristics as the NTCDI composition increased".

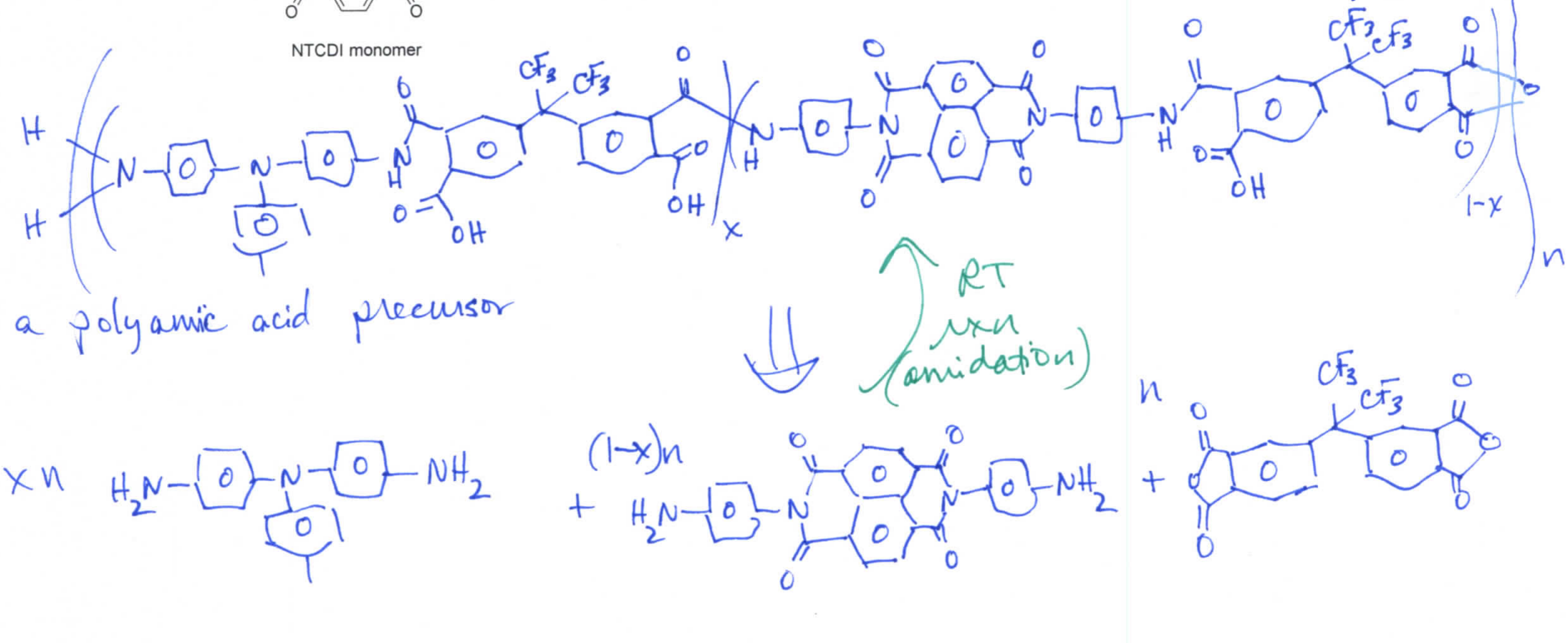


Δ (*)

(a) Provide a retrosynthetic pathway by which this copolymer structure could be prepared. To avoid confusion, please note that the 6-membered ring imides are part of the NTCDI monomer, which is shown below. **[10 points]**



NTCDI monomer



[1] Kurosawa, T.; Lai, Y.-C.; Yu, A.-D.; Wu, H.-C.; Higashihara, T.; Ueda, M.; Chen, W.-C. Effects of the Acceptor Conjugation Length and Composition on the Electrical Memory Characteristics of Random Copolyimides", *J. Polym. Sci, Part A: Polym. Chem.* **2013**, *51*, 1348-1358.

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(b) State whether this copolyimide is a random/statistical copolymer or a block copolymer. **[2 points]**

random/statistical copolymer

(c) State whether the polymerization step of your retrosynthesis would proceed by a chain-growth or step-growth process. **[2 points]**

step-growth

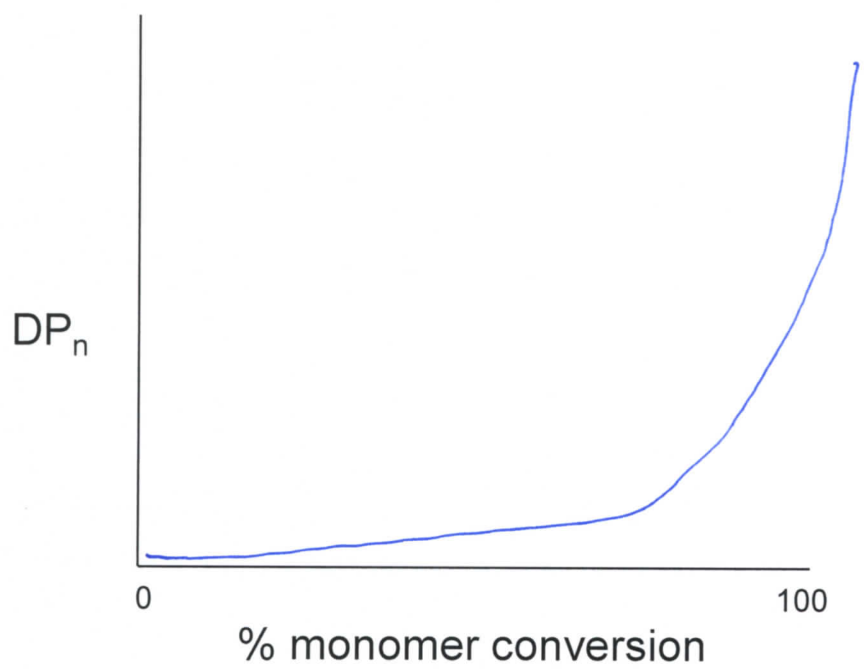
(d) State whether your polymerization would be controlled or un-controlled. **[2 points]**

un-controlled

(e) State whether the molecular weight distribution would be expected to be narrow or broad. **[2 points]**

broad

(f) Draw the expected DP_n *vs.* % monomer conversion plot on the axes below. **[4 points]**



(g) Predict the thermal characteristics for this polymer, in terms of thermal transition temperature(s) and thermal decomposition temperature(s), and explain. **[4 points]**

high T_g + T_m (if xtalline), e.g. not observable before decomp.
+ high decomp. temp., e.g. > 500 °C
b/c of rigid backbone comprised of aromatic rings + imide linkages

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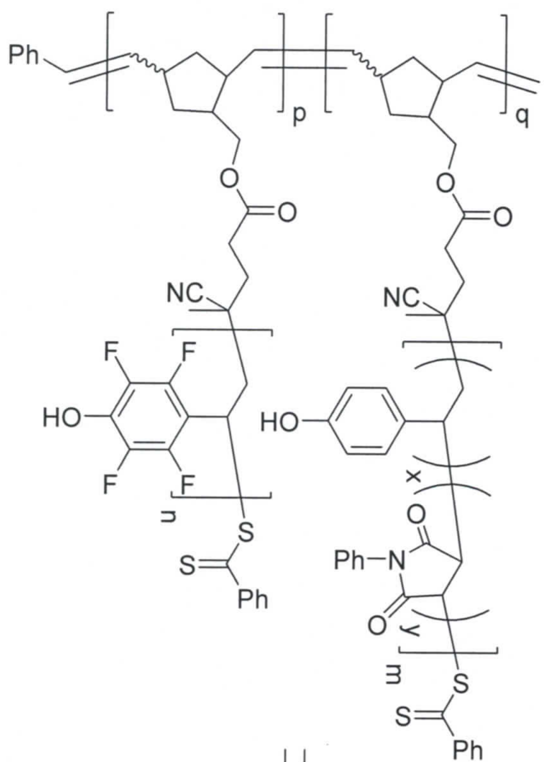
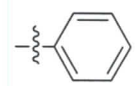
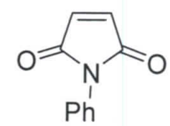
2. As promised during lecture, this question requires that you provide a retrosynthetic analysis for the following molecular brush, which is prepared by a combination of RAFT polymerization and ROMP. Please note a few points: i) the termination step was not shown explicitly during the discussion of this molecular brush, but was illustrated during the final lecture of the course; ii) the chemical structure for N-phenylmaleimide is given and may be of use; iii) although the mechanism for RAFT polymerization was illustrated during lecture for a trithiocarbonate chain transfer agent, the mechanism is the same for the dithioester functionality.

(a) Provide a retrosynthetic pathway for the preparation of this molecular brush (your answer can continue onto the next page). **[15 points]**

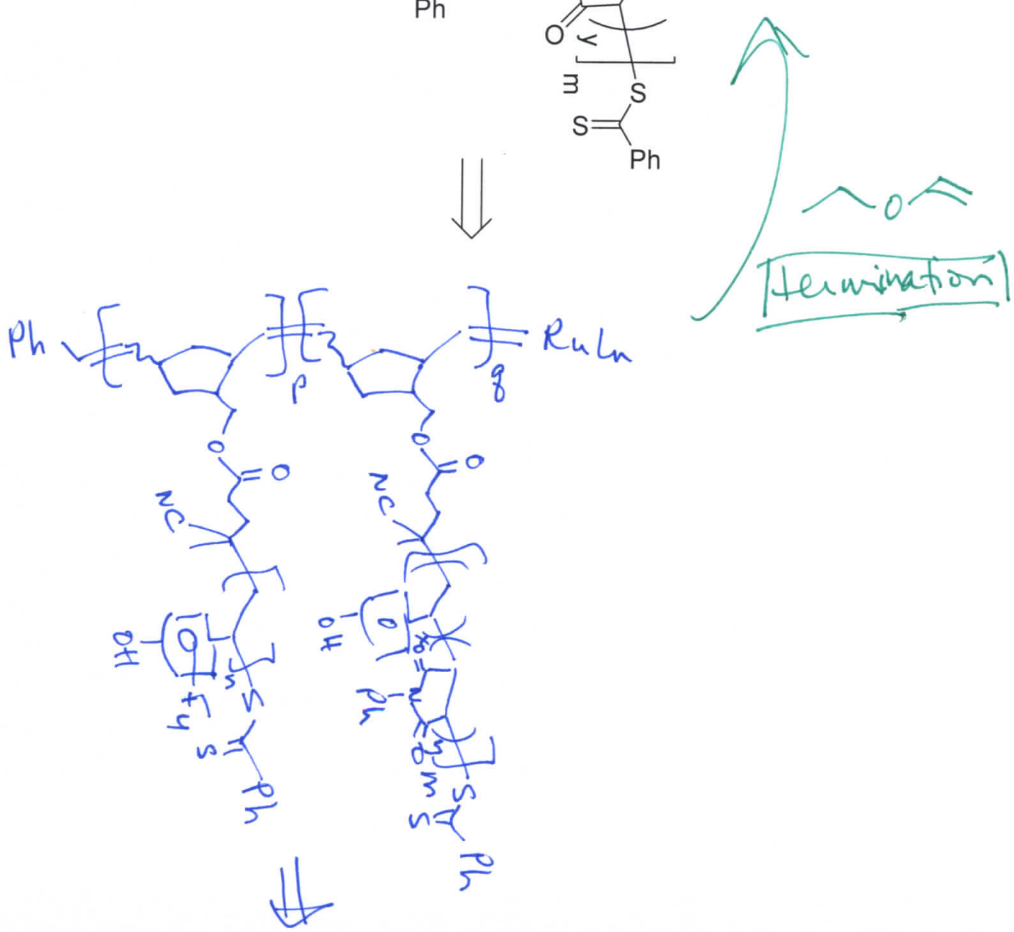


x = y = 0.5

Ph = phenyl = 



N-phenylmaleimide



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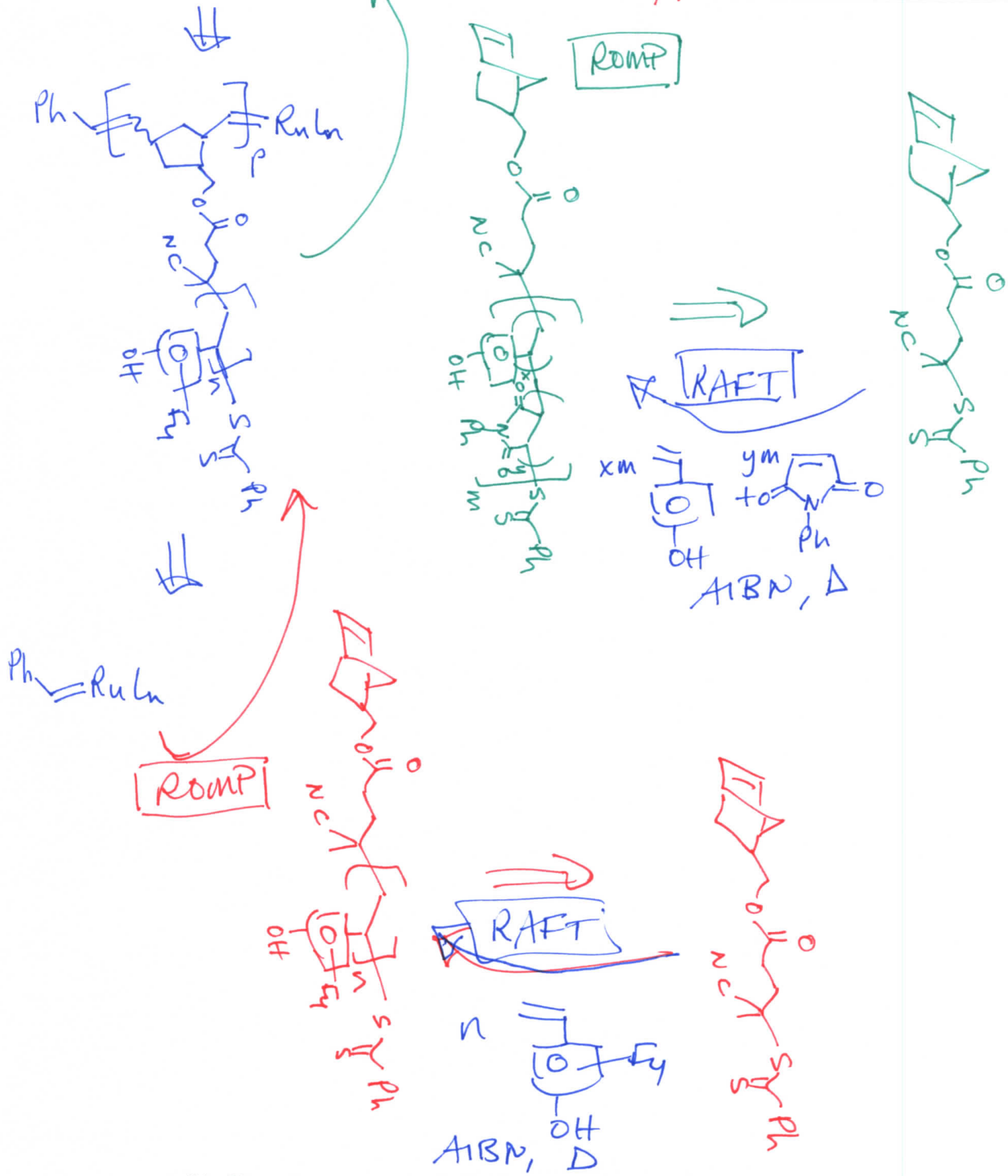

(b) Given that x = y = 0.5 for the copolymer graft, predict the reactivity ratio values for the copolymerization of *p*-hydroxystyrene (1) and N-phenylmaleimide (2). **[2 points]**

r_1 = ~0

r_2 = ~0

} alternating copoly

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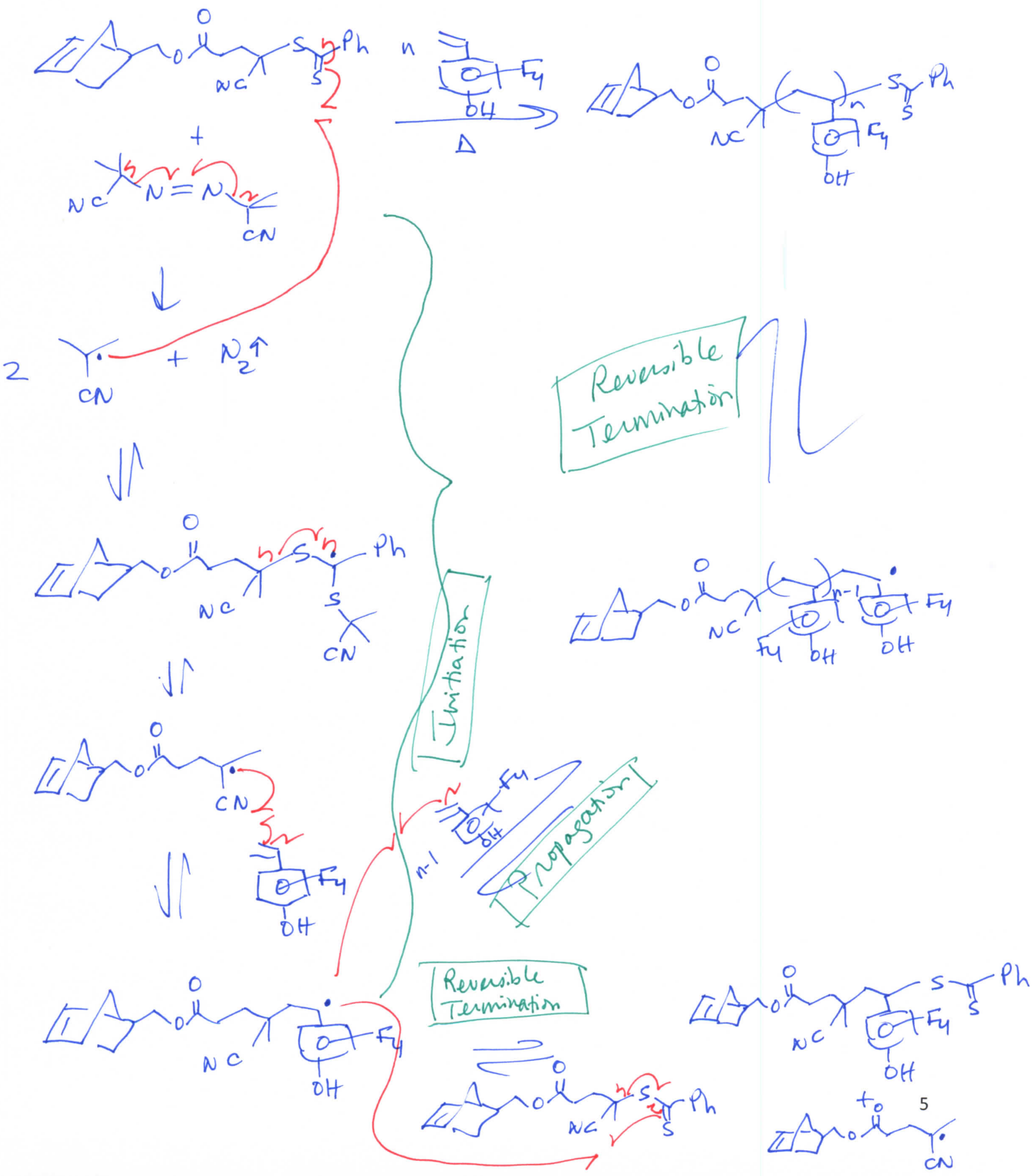
(c) Choose one of your RAFT polymerization steps and draw the electron arrow-pushing mechanism for the RAFT polymerization, labeling all initiation, propagation and (reversible) termination steps. **[6 points]**



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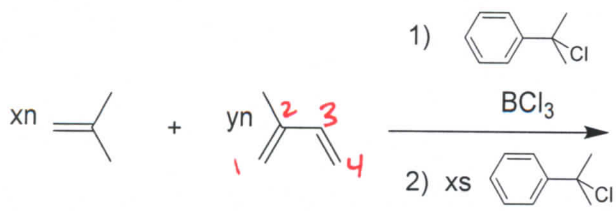
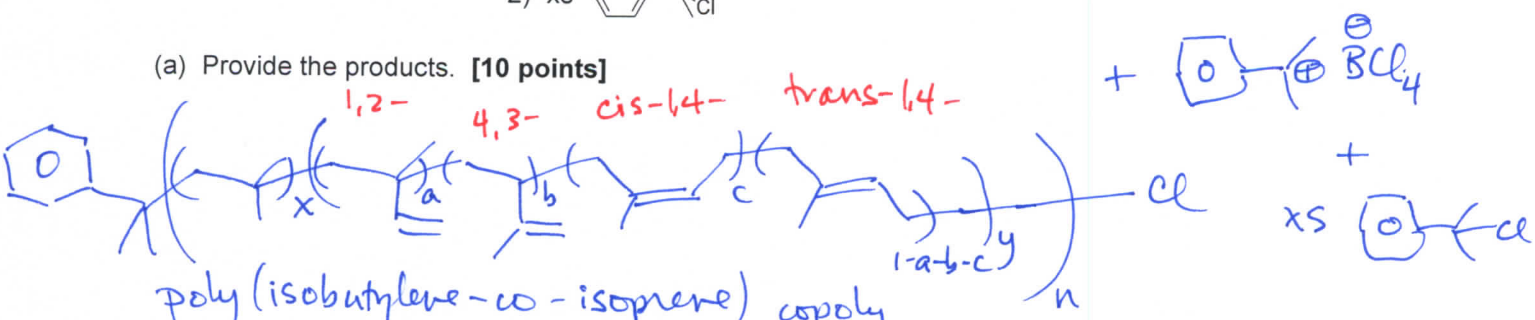
3. For the following cationic chain-growth, addition copolymerization:



(a) Provide the products. **[10 points]**



poly(isobutylene-co-isoprene) copoly

(b) State which regioisomer for the isoprene repeat units is favored, and state and illustrate mechanistically the reason for your answer. **[5 points]**

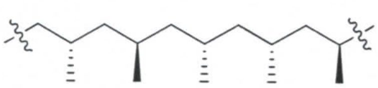
1,2- most favored
b/c allylic
3° carbocation
intermediate

(c) State at least one product in which this copolymer could be found, *e.g.* name the item that was shown during lecture. **[2 points]**

butyl rubber tubing

4. (a) For the following polypropylene segments, label their tacticities and predict whether they are likely to pack into crystalline or amorphous domains. **[12 points]**

 isotactic — xtalline

 atactic — amorphous

 syndiotactic — xtalline

(b) Describe the key features of the system that we discussed as being used by Dow to obtain olefin block copolymers with alternating semicrystalline and amorphous segments. **[6 points]**

2 catalysts — 1 gives xtalline segment
1 gives amorphous segment
+
chain shuttling agent — reversibly transfers chain between cat. + shuttling agent

} polym by 2 catalysts w/ shuttling of chains provides for alternating segments of any given chain as being xtalline + amorphous

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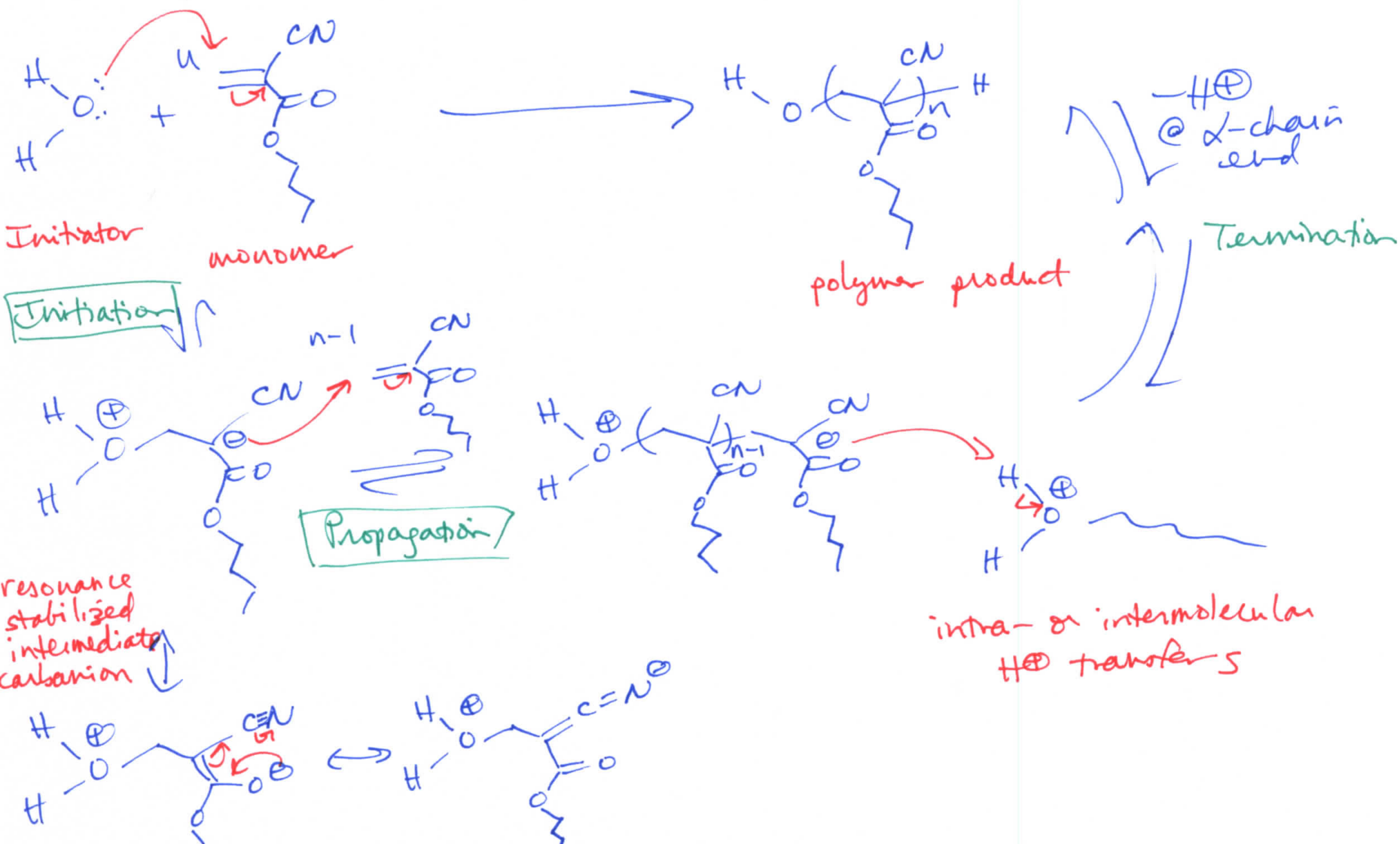
5. For quiz #10, several students expressed interest in the broad range of applications for super glue, including those beyond typical daily applications, *e.g.* in the medical field, forensics, *etc.*, and requested that a final examination question involve super glue. Therefore,

(a) provide the chemistry for any version of an α-cyanoacrylate "super glue", including the monomer, initiator, mechanism of polymerization and the final polymer product structure; **[12 points]**



(b) state what kind of polymerization is involved; **[2 points]**

anionic chain-growth, addition polym

(c) state why this polymerization does not proceed while the monomer is stored in a closed tube. **[2 points]**

water or another nucleophile is required to serve as an initiator

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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