Name: ANSWER KEY [printed]

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

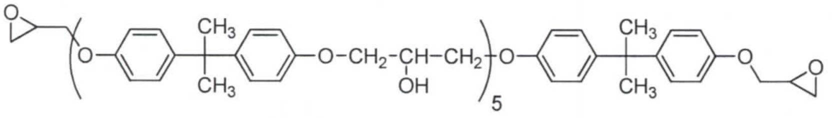
________________________ [signature]

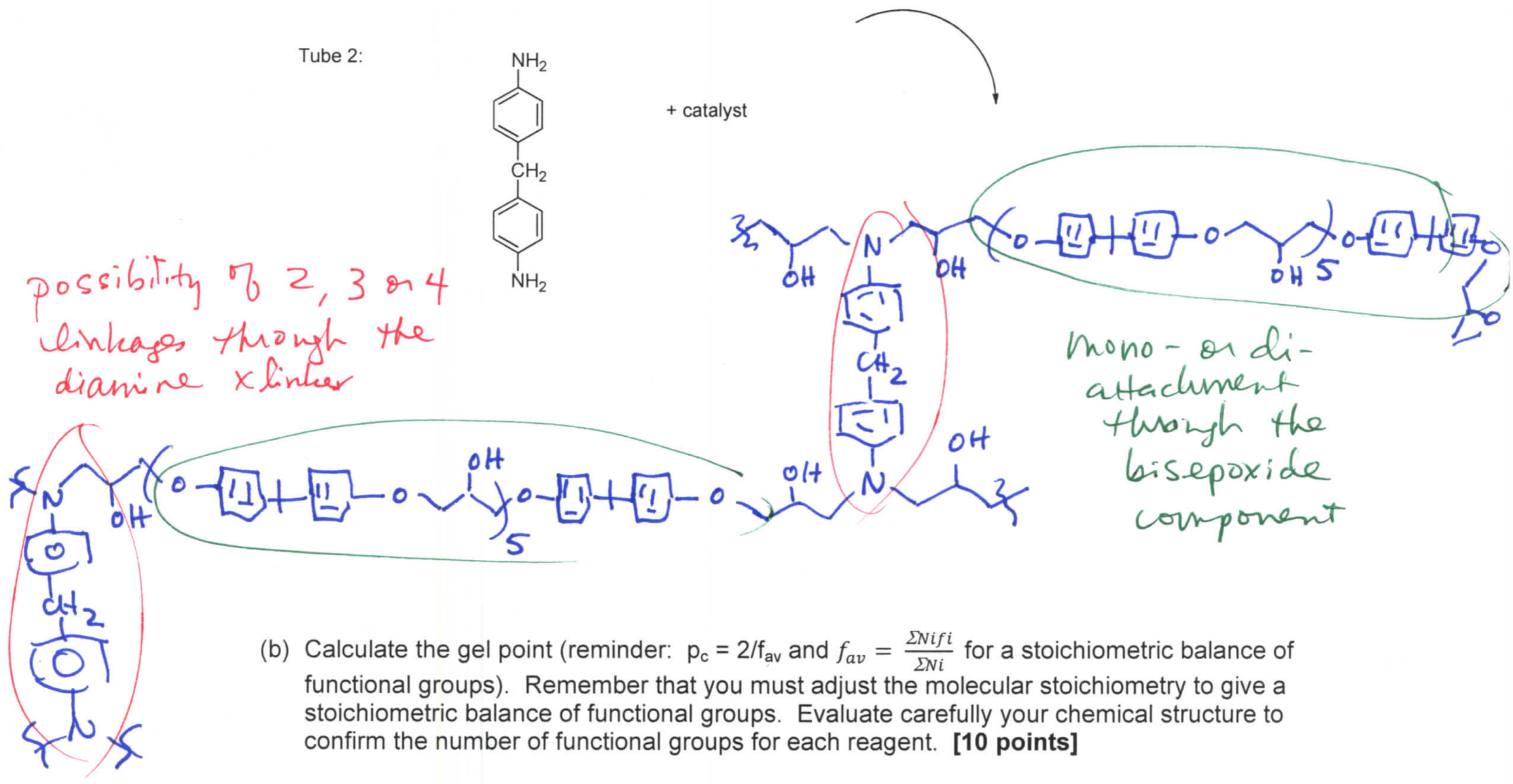
Final Exam, May 6, 2011, 200 pts
Polymer Chemistry, CHEM 466, Spring 2011
Texas A&M University, College Station, TX, USA

1. For the reaction of the epoxy components shown below:

   (a) Draw the chemical structure for the crosslinked network product. **[10 points]**

Tube 1:





possibility of 2, 3 or 4 linkages through the diamine xlinker

mono- or di- attachment through the bisepoxide component

(b) Calculate the gel point (reminder: $p_c = 2/f_{av}$ and $f_{av} = \frac{\Sigma N i f i}{\Sigma N i}$ for a stoichiometric balance of functional groups). Remember that you must adjust the molecular stoichiometry to give a stoichiometric balance of functional groups. Evaluate carefully your chemical structure to confirm the number of functional groups for each reagent. **[10 points]**

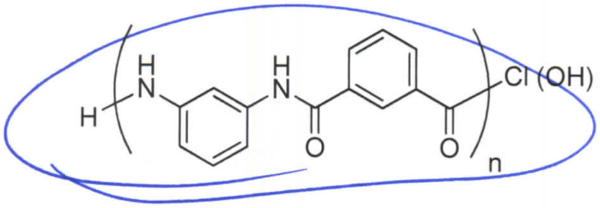
Tube 1, $f_i = 2$; Tube 2, $f_i = 4$
$\Rightarrow N_i = 2$; $\Rightarrow N_i = 1$ } for stoichiometric equiv. of functional groups

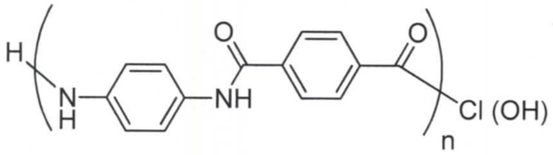
$$\Rightarrow f_{av} = \frac{2 \cdot 2 + 1 \cdot 4}{2+1} = \frac{8}{3} \quad \Rightarrow p_c = 0.75$$

= 75% conversion of func. groups

Name: ANSWER KEY [printed]

2. (a) Circle the one of the following two polymers that is most likely to be found as a woven fiber in heat-resistant fabric products, *e.g.* gloves, jackets, pants, with the tradename Nomex, and provide a brief rationale for your selection. **[10 points]**

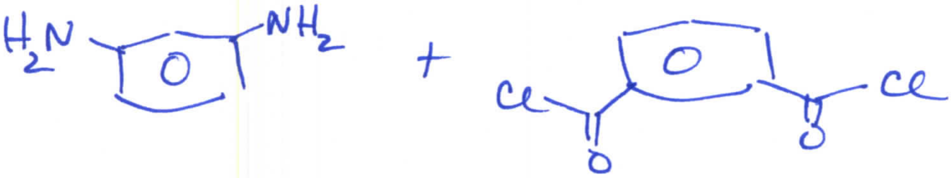




The rigid, stable aromatic rings and amide linkages give both polymers the properties of high strength, high thermal transition temperatures, and high thermal stabilities, but the meta-substituted aromatic rings reduce the crystallinity & give increased flexibility for fabric applications.

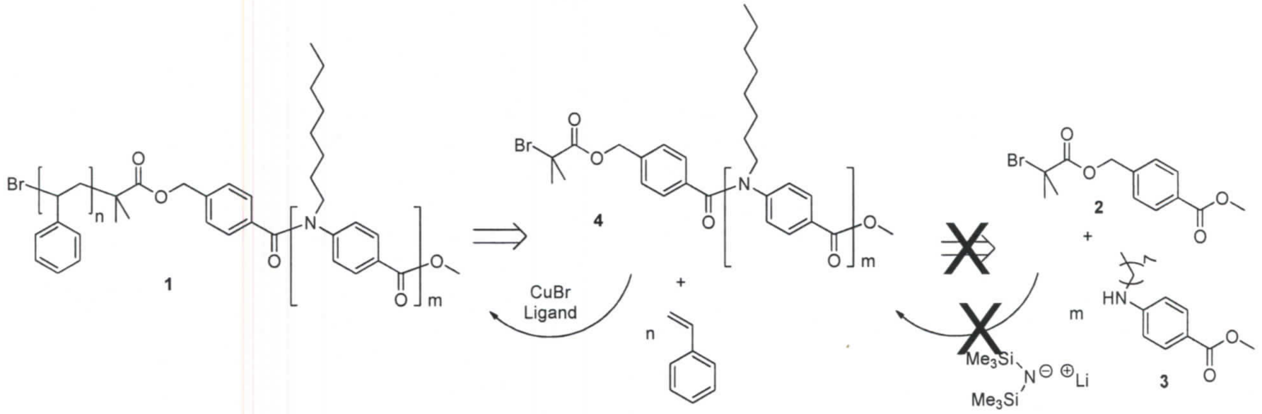
Base

(b) Provide an example of monomer(s) from which Nomex could be produced. **[10 points]**

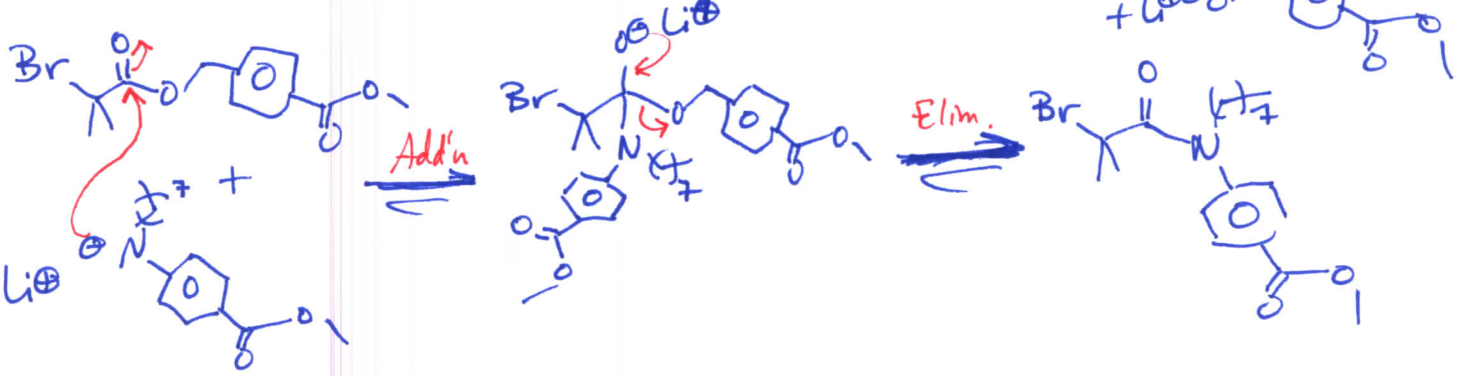


Name: ANSWER KEY [printed]

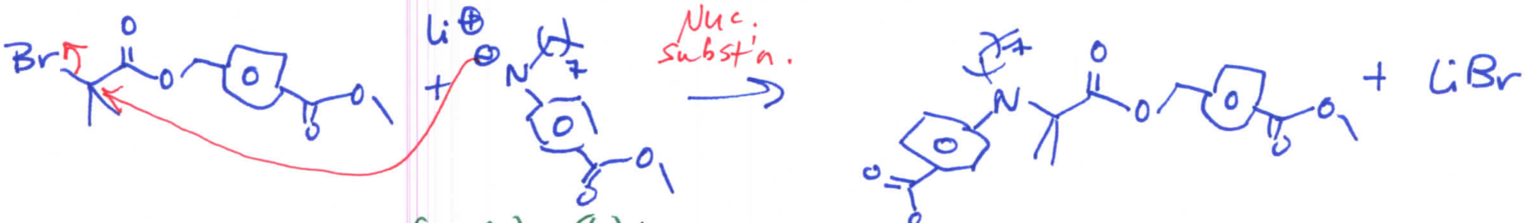
3. In 2010, Yokozawa's laboratory produced interesting diblock copolymers, **1**, containing a block segment of polybenzamide structure and a block segment of polystyrene, *via* a combination of chain-growth condensation polymerization and atom transfer radical polymerization (Huang, C.-F.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2948-2954). Initially, their synthetic approach began from a bifunctional initiator, **2**, which contained both a methyl benzoate group to initiate chain-growth condensation polymerization of monomer **3** in the presence of lithium hexamethyldisilazide as a strong base, and an alkyl bromide to initiate atom transfer radical polymerization of styrene. Unfortunately, the chain-growth condensation polymerization failed to provide controlled polymerization conditions to afford **4** (as represented by the X's through the retrosynthetic arrow and the forward synthetic reaction arrow). Instead, "low monomer conversion (21%) and tailing GPC traces were obtained using initiator **2**".



(a) Draw an electron arrow-pushing mechanism for a potential side reaction with **2** that could lead to the observed quenching of the deprotonated, aminyl anion of monomer **3** and give the structures for the resulting side products. **[10 points]**



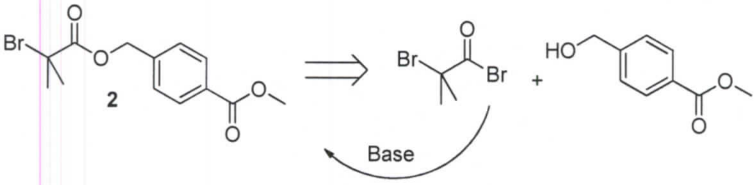
(b) Draw a second electron arrow-pushing mechanism for another potential side reaction with **2** that could lead to the observed quenching of the deprotonated, aminyl anion of monomer **3** and give the structures for the resulting side products. **[10 points]**

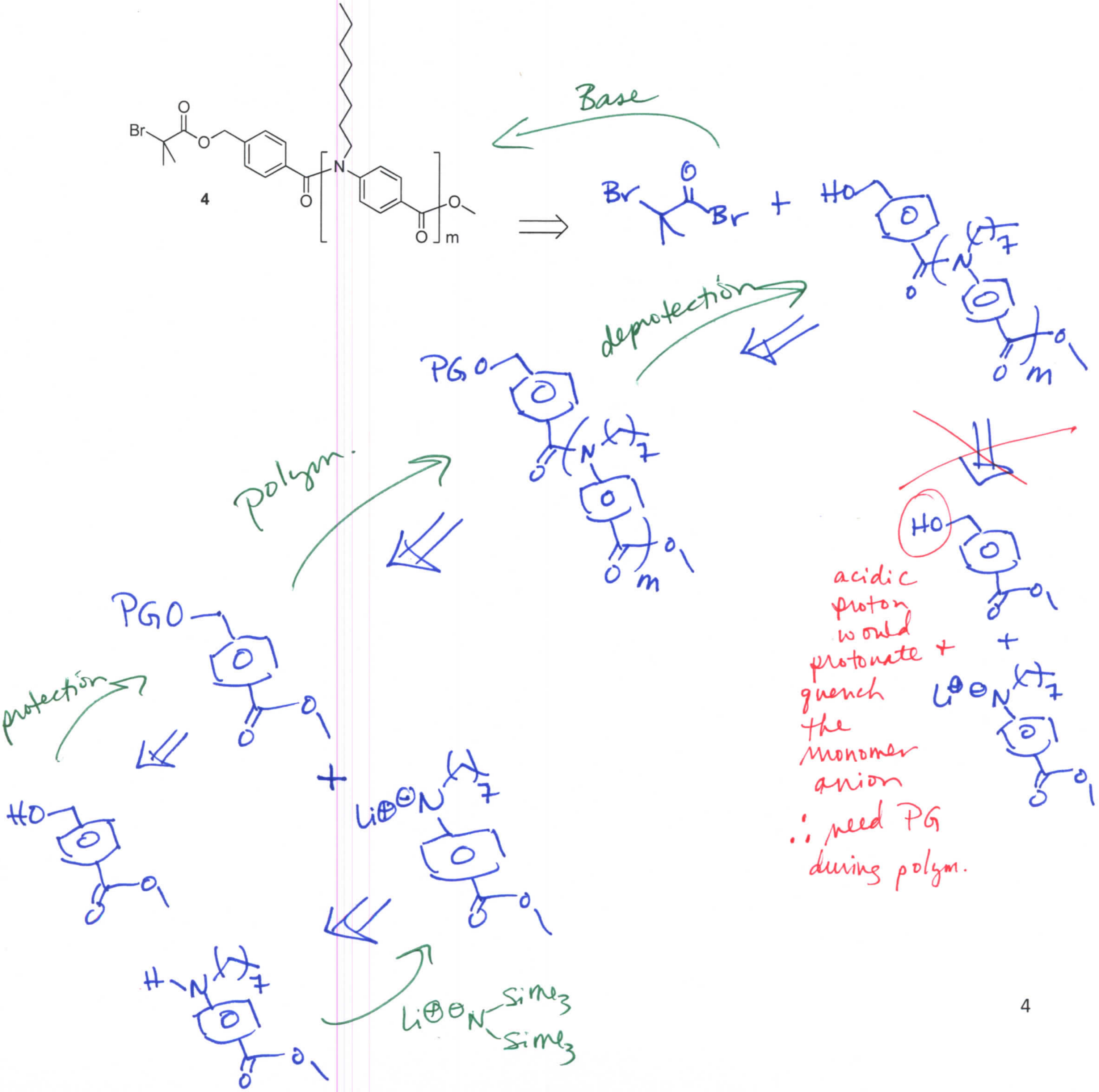


Another correct answer for (a) or (b):

Name: ANSWER KEY [printed]

(c) The initiator **2** can be prepared by the retrosynthetic step shown below. Given this information, provide an alternate retrosynthetic pathway to produce **4**. Be certain to consider possible side reactions, and potential need for protecting groups, as you devise your retrosynthesis. If you choose to use a protecting group, a generic "PG" label and a generic "deprotection" step can be used. **[10 points]**

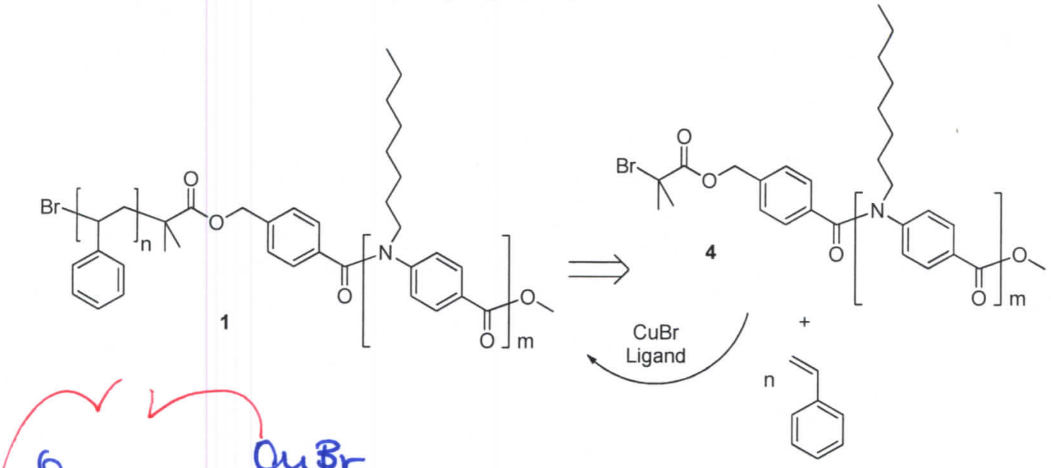

2

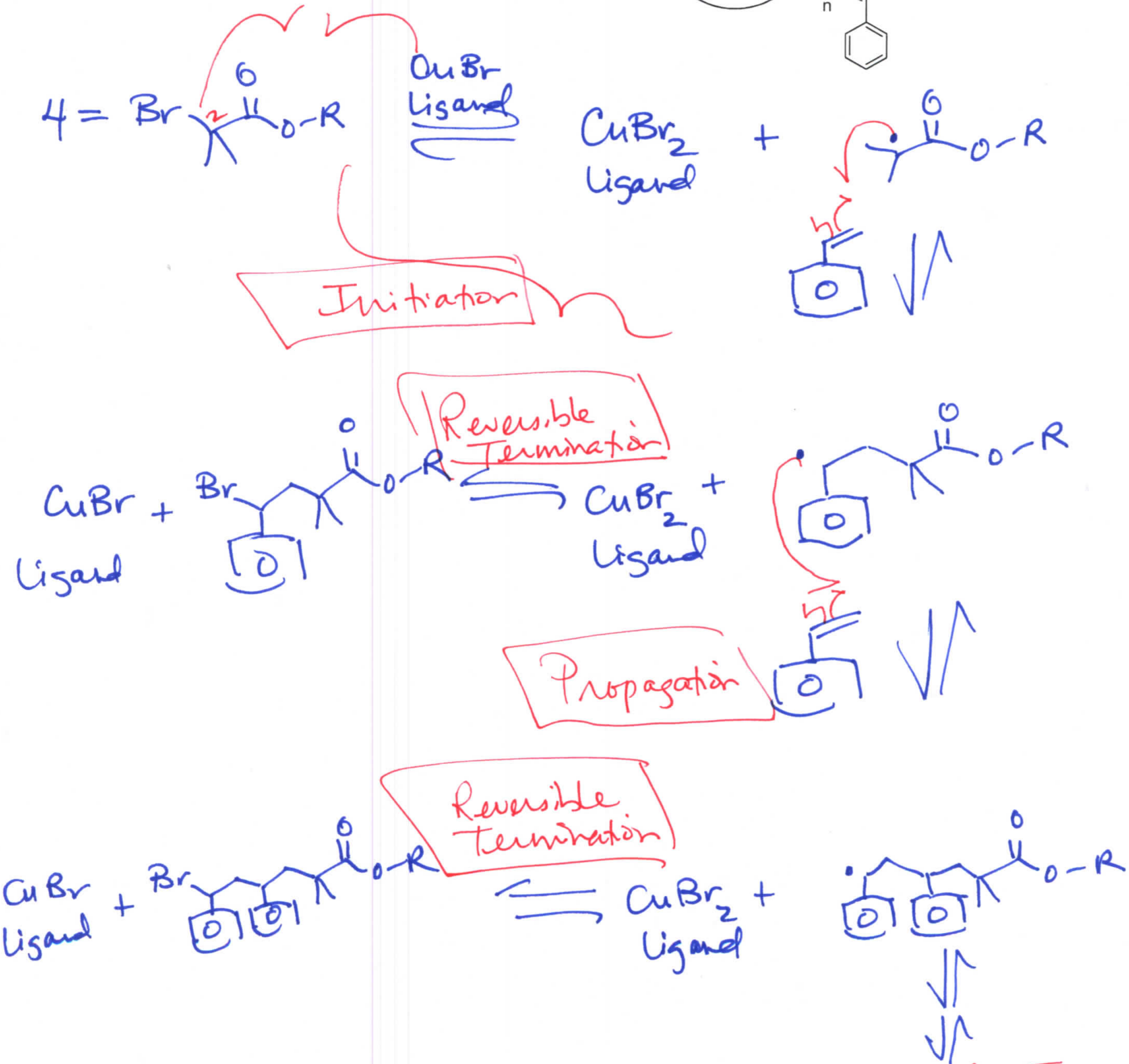

4

acidic proton would protonate + quench the monomer anion ∴ need PG during polym.

Name: ANSWER KEY [printed]

(d) Provide the electron arrow-pushing mechanism for the atom transfer radical polymerization of styrene as a chain extension from **4**, serving as a macroinitiator, to afford **1**. Label any initiation, propagation and termination steps. **[20 points]**

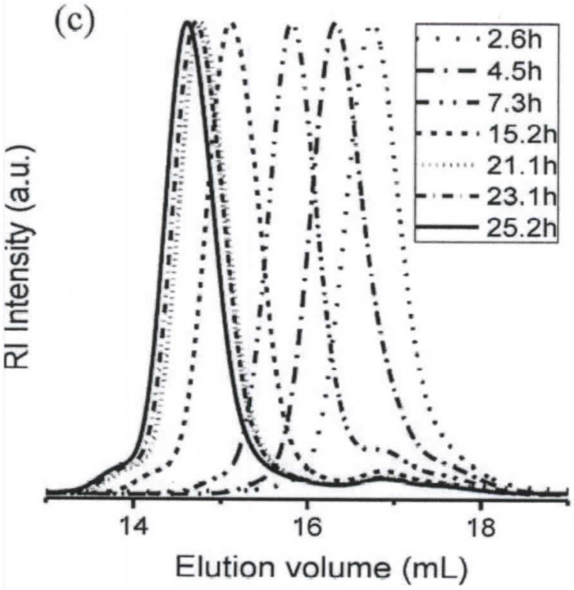




Repeated Prop. + Rev. Term. to build polymer

Name: ANSWER KEY [printed]

(e) Explain what is being observed in the following overlaid size exclusion chromatography (SEC) traces that were collected as a function of time during the atom transfer radical polymerization of styrene as a chain extension from **4** to give the final block copolymer **1**. **[10 points]**



As time increases, the elution volume of the polymer decreases, indicating polymer chain growth.

(f) What is the significance of the residual peak at *ca.* 16.9 mL and how does it relate to your retrosynthetic pathway of part (c)? **[5 points]**

The residual peak @ 16.9 mL is likely due to initial polybenzamide chains, analogs of 4, but lacking the initiating chain end. According to the retrosynthesis of (c), these polybenzamides would have failed to undergo either the deprotection or esterification reactions.

Name: ANSWER KEY [printed]

4. Given data from your textbook Table 5.1, indicating that styrene and vinyl chloride exhibit reactivity ratios $r_1 = 17$ and $r_2 = 0.02$ as comonomers M_1 and M_2, respectively, undergoing radical copolymerization, and Figure 5.1 below:

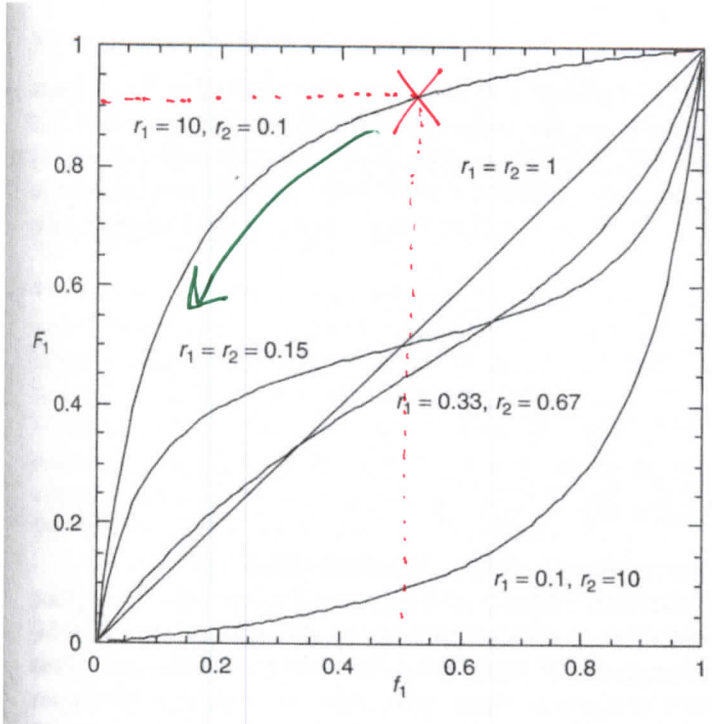


Figure 5.1 Mole fraction of component 1 in the copolymer as a function of feedstock composition for various reactivity ratios.

(a) Indicate, with an X drawn at the point on the most relevant plot within Figure 5.1 above, the mole fraction of M_1 that would be incorporated into the initial copolymer formed at an initial feedstock of a stoichiometric equivalence of the two monomers. **[5 points]**

(i.e. $f_1 = 0.5$) $\Rightarrow F_1 = 0.9$

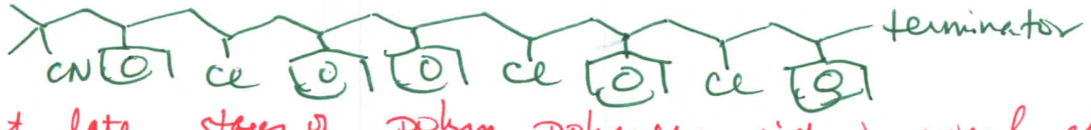
(b) Indicate, with an arrow drawn along the most relevant plot within Figure 5.1 above, the direction of change for the mole fraction of M_1 that would be incorporated into later copolymers formed as M_1 is consumed. **[5 points]** F_1 decreases as f_1 decreases

(c) Predict the overall copolymer composition(s), qualitatively, by drawing the expected polymer structure(s) that would result using a stoichiometric equivalence of the two comonomers and azobisisobutyronitrile (AIBN) as the initiator, with the copolymerization proceeding to *ca.* complete conversion of the comonomers. **[10 points]**

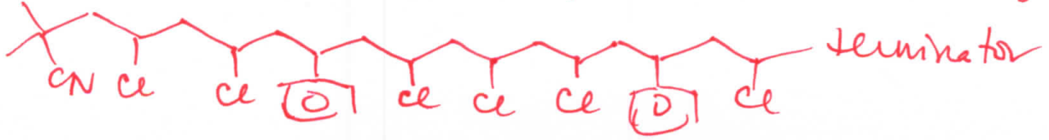
mixture of polys of Δ composition
+ relatively broad PDI, w/overall ≈ 50%
of each monomer
incorporated

at early degrees of monomer conversion, polymers rich in styrene:

at later stages of polym; increasing amts of vinyl chloride:

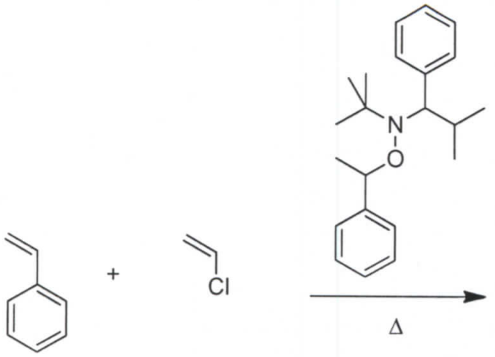


at late stages of polym, polymers rich in vinyl chloride:



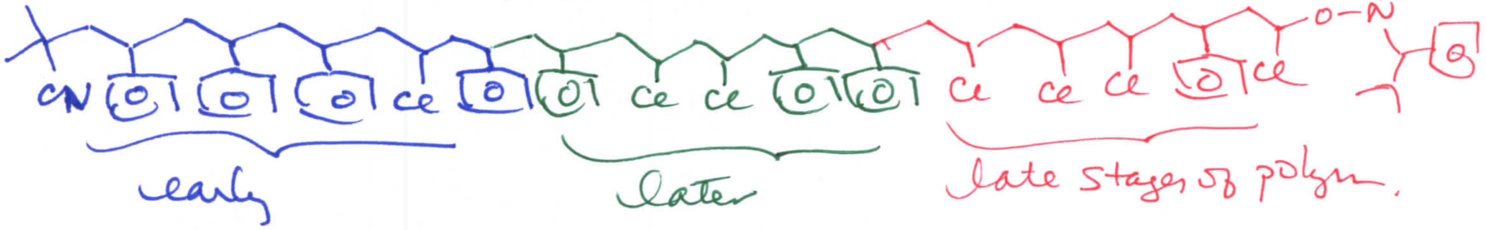
Name: ANSWER KEY [printed]

(d) Predict the overall copolymer composition(s), qualitatively, by drawing the expected polymer structure(s) that would result using a stoichiometric equivalence of the two comonomers and the alkoxyamine shown below as the initiator, with the copolymerization proceeding to *ca.* complete conversion of the comonomers. **[10 points]**

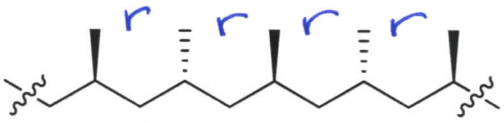


all polys of same composition w/ ΔF_1 along the poly backbone + all narrow PDI, w/overall ca. 50% of each monomer incorp.

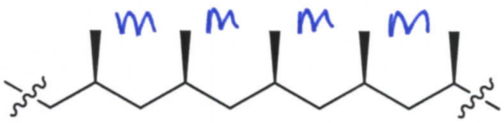
rich in styrene progressing to rich in vinyl chloride



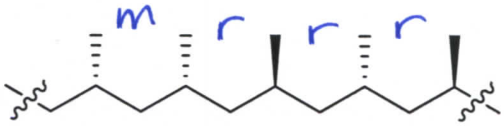
5. For each of the following polypropylene chain sequences, label each diad as meso, "m", or racemic, "r", and identify each type of tacticity. **[30 points]**



syndiotactic



isotactic



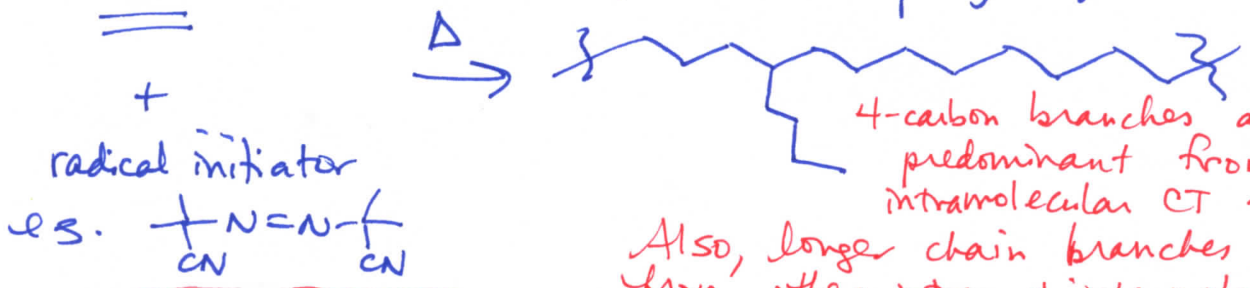
atactic

Name: ANSWER KEY [printed]

6. Propose synthetic routes, giving reaction sequences that include the monomer(s) and any initiator(s) or catalyst(s) that could be used to prepare low density polyethylene (LDPE) and high density polyethylene (HDPE). Draw the polymer backbones of LDPE and HDPE. In this one instance, you are not required to show termination steps or the polymer chain ends.

(a) LDPE: **[10 points]**

branched polyethylene

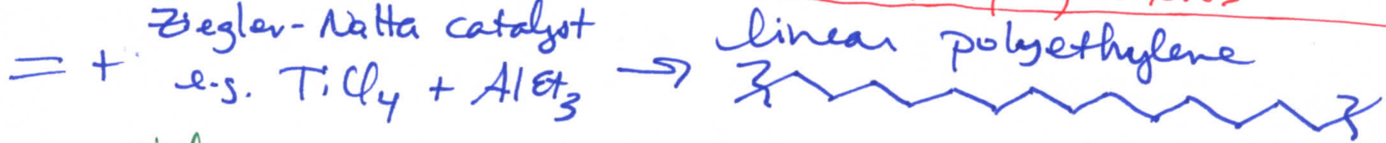


4-carbon branches are predominant from intramolecular CT to poly

Also, longer chain branches originate from other intra- + intermolecular CT to poly rxns

(b) HDPE: **[10 points]**

linear polyethylene



alternatively:

(c) Give an experimental technique that could be employed for quantitative characterization of each of the following properties, and indicate the feature(s) that would distinguish the LDPE and HDPE samples (*i.e.* what differences in the data would be used to determine and differentiate the PE structures?).

(i) thermal transition temperatures (*i.e.* T_g, T_{crys}, T_m) **[5 points]**

differential scanning calorimetry (DSC) — higher relative + absolute intensities of the endothermic T_m + exothermic T_c expected for the HDPE

(ii) degree of branching **[5 points]**

NMR spectroscopy — det'n branching for LDPE from measurement of branching + terminal ($CH + CH_3$) vs. linear (CH_2) units

(iii) molecular weight **[5 points]**

size exclusion chromatography, viscometry, osmometry, light scattering, or MALDI-TOF — expect higher MW for Ziegler-Natta catalyzed polym, unless intentionally terminated by add'n of H_2 during polym.

Equations, which may be of use:

Number-average molecular weight:

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

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

Weight-average molecular weight:

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

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

Degree of polymerization:

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

c = extent of conversion of functional groups

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

Polydispersity index:

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

Critical extent of reaction:

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

Average degree of monomer functionality:

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

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