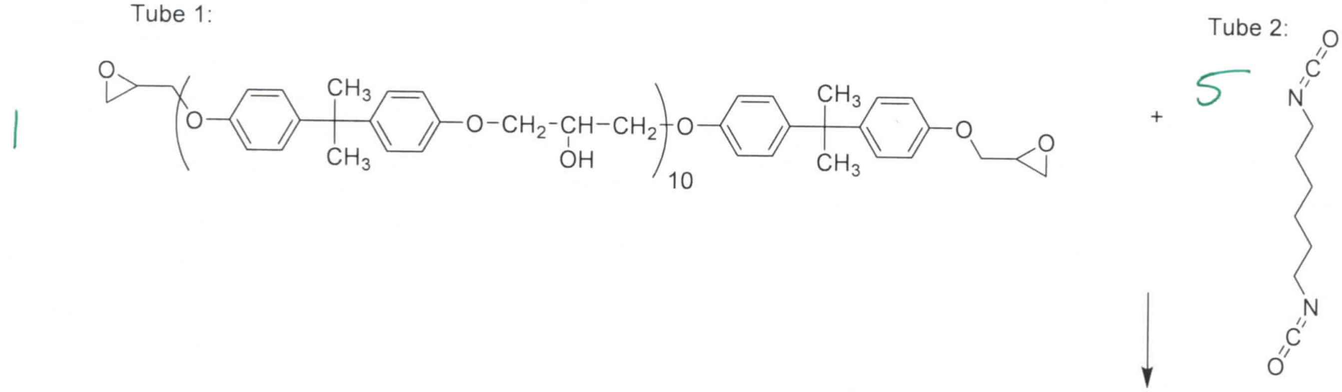
Name: ANSWER KEY [printed]

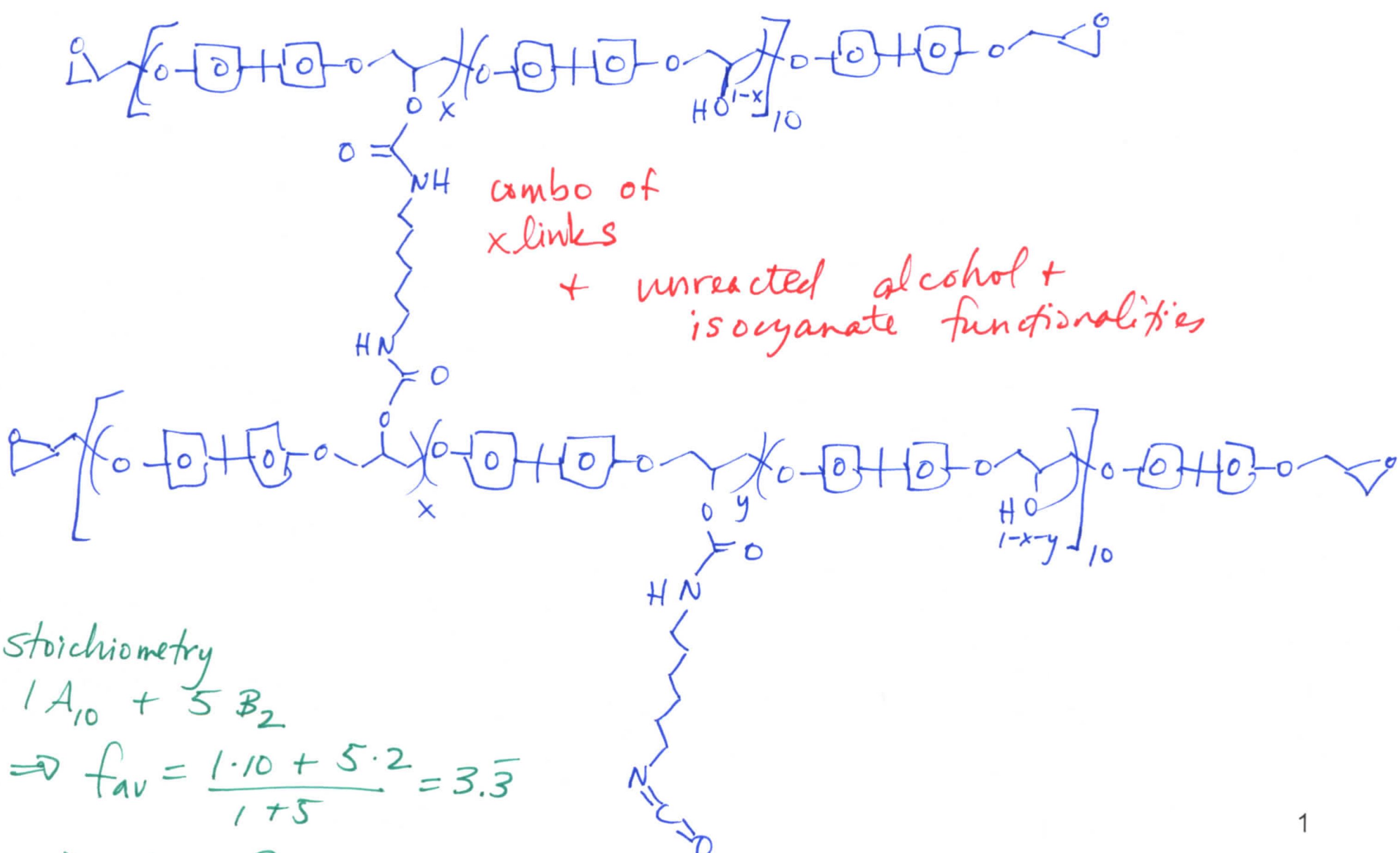
"On my honor, as an Aggie, I have neither given nor received unauthorized aid on this academic work."

________________________ [signature]

Exam II, March 6, 2014, 100 pts
Polymer Chemistry, CHEM 466, Spring 2014
Texas A&M University, College Station, TX, USA

1. For the reaction of the epoxy components shown below, draw the chemical structure for the crosslinked network product (8 points) and 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) (8 points).





stoichiometry

$1 A_{10} + 5 B_2$

$\Rightarrow f_{av} = \frac{1 \cdot 10 + 5 \cdot 2}{1 + 5} = 3.\bar{3}$

$\Rightarrow p_c = \frac{2}{3.3} = 0.6 = 60\%$ conversion to reach gel pt.

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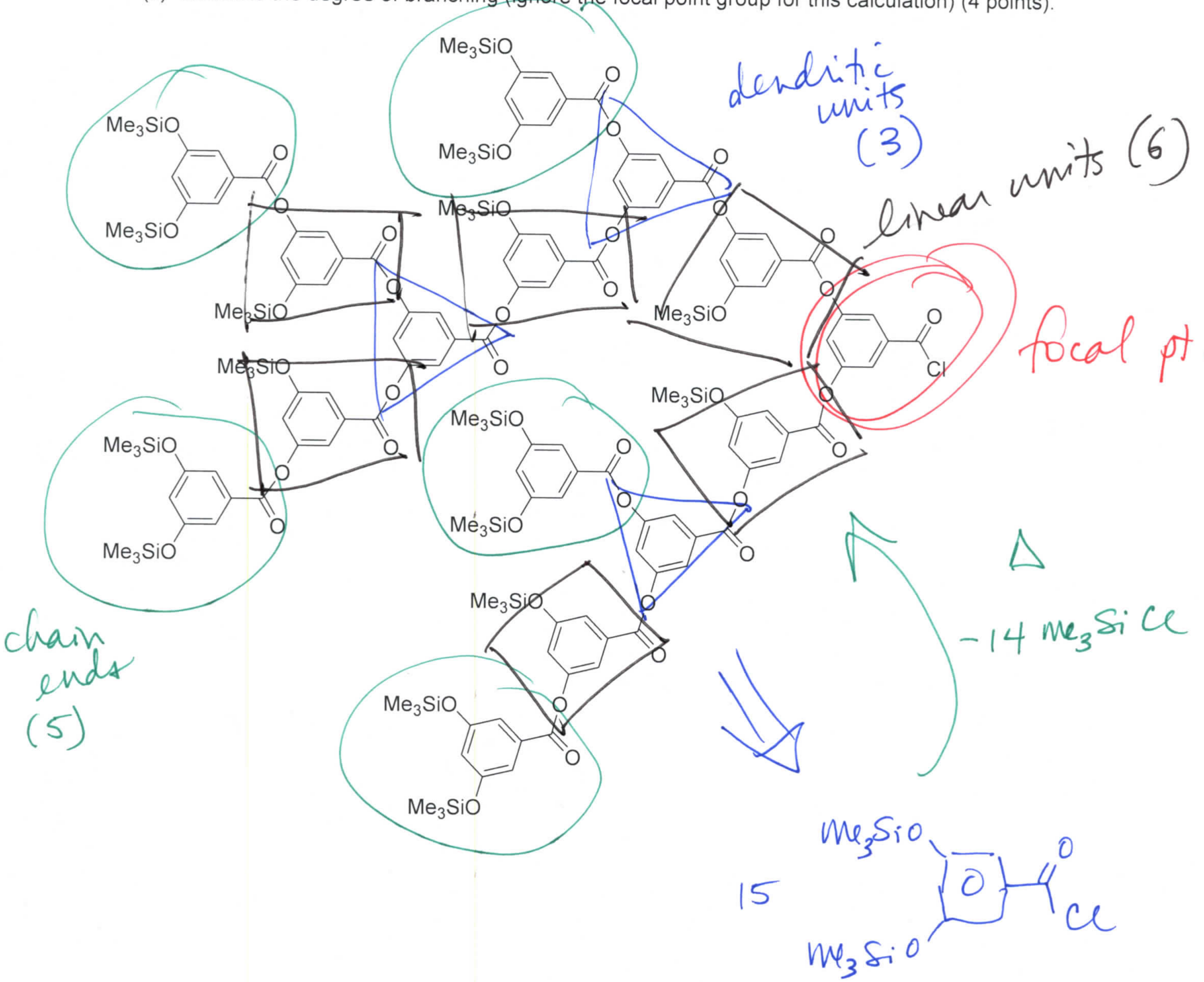
2. For the hyperbranched polyester structure shown below:
   (a) provide a retrosynthetic analysis (don't forget to draw any retrosynthetic arrows needed for your answer) (4 points);
   (b) label each type of repeat unit, and also draw circles around the chain ends, triangles around the dendritic units, rectangles around the linear units, and a double circle around the focal point (8 points);
   (c) calculate the degree of branching (ignore the focal point group for this calculation) (4 points).



$$DB = \frac{\#\,\text{dendritic} + \text{ends}}{\#\,\text{dendritic} + \text{ends} + \text{linear}}$$

$$= \frac{3+5}{3+5+6} = 0.57 = 57\% \text{ or } 60\%$$

(rounded to 1 sig figs)

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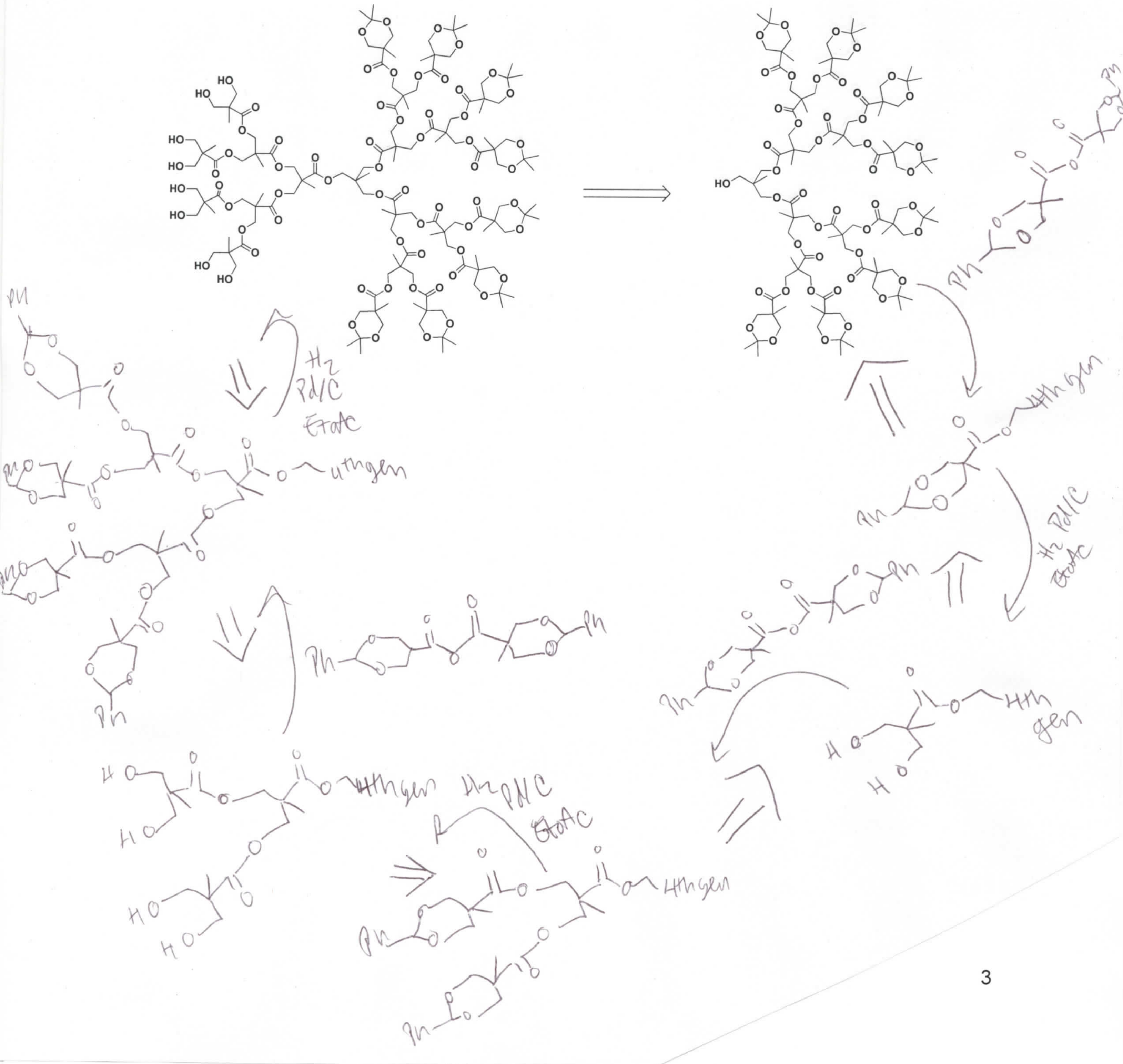
3. The dendritic structures shown below were synthesized by Lee *et al.* (Lee, C.; Gillies, E. R.; Fox, M. E.; Gillaudeu, S. J.; Fréchet, J. M. J.; Dy, E. E.; Szoka, F. *Proc. Nat. Acad Sci.* **2006**, *103*, 16649-16654) in order to produce a complex drug delivery system for the treatment of cancer. The 4th generation dendron, which comprises the right side of the structure on the left side of the page, was synthesized in a convergent manner that was finalized by attachment to and deprotection of the core, to afford a 4th generation arm (right side of page). The 3rd generation dendron (left side of the structure on the left side of the page) was then grown from the prefabricated 4th generation arm in a divergent manner. Provide a retrosynthetic analysis for the construction of the 3rd generation dendron (left side of dendritic structure). You should work back to the 4th generation dendron as shown below. [12 points]



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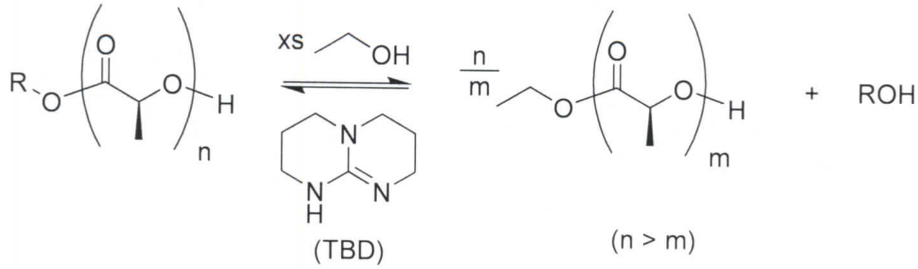
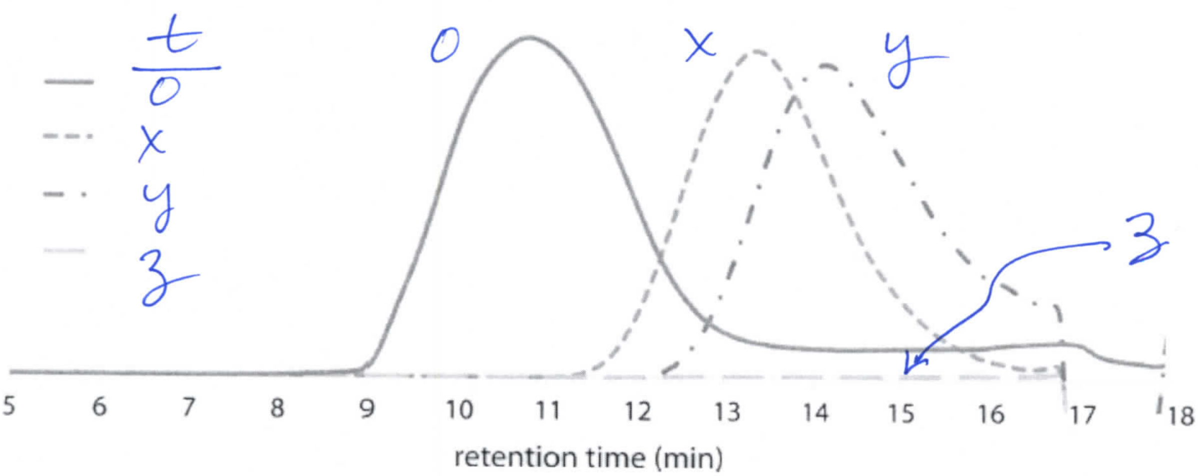
4. The following questions are related to the reaction of polylactide with ethanol in the presence of TBD as an organocatalyst, as shown below and reported in F. A. Leibfarth *et al.* *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 4814-4822.



(a) Explain what is being observed (in terms of what is occurring chemically) by the series of GPC traces shown below, from a reaction of polylactide with 3n molar equivalents of ethanol and 0.01n TBD. [4 points]

depolymerization by organocatalyzed transesterification reactions



(b) Label each of the four GPC traces (either at the legend or on the traces directly) with the reaction time at which it would have been acquired, as t = 0, x, y, and z, where reaction time increases from 0 < x < y < z. [8 points]

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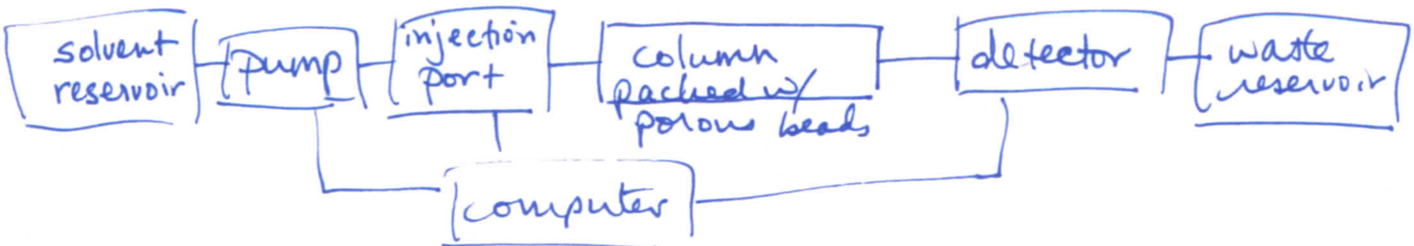
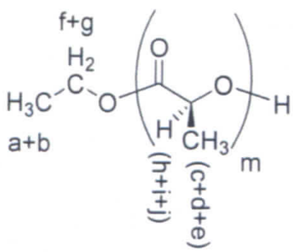
(c) Draw a schematic illustration of the components that comprise a GPC system. [14 points]



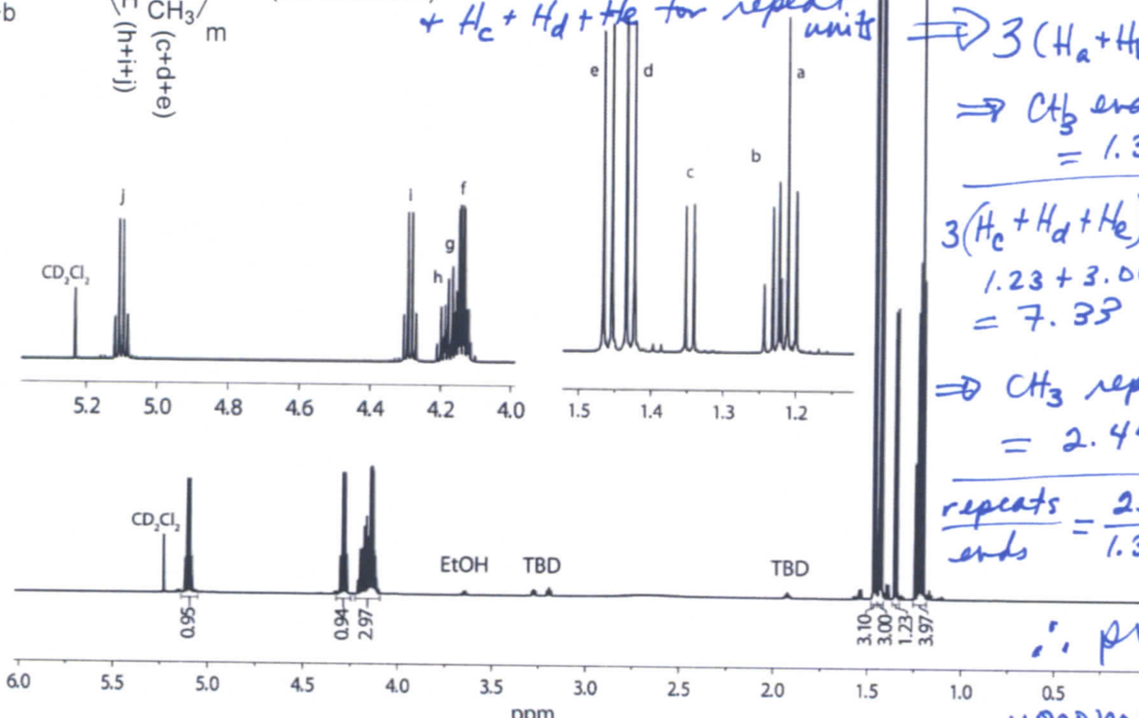
(d) Indicate the parameter that determines the retention time that a molecule experiences during analysis by GPC, how the magnitude of the value for that parameter affects the retention time, and why. [6 points]

hydrodynamic volume, V_h; as V_h increases, retention time decreases; larger molecules are excluded from higher #'s of pores, so diffuse into + out of fewer pores + reside in the column for a shorter time

(e) Given the [1]H NMR spectrum below, calculate the average degree of polymerization, m. A few notes: there are 2 inset spectra that are simply expanded views of regions of the entire spectrum (note the scale to identify the regions); integrals are not drawn on the spectrum, rather the integration values are given below each set of peaks; there are multiple signals (sets of peaks) for each type of proton of the structure, so please review carefully the assignments that are made on the structure; recall the reaction that generated this sample—it makes the problem a bit tricky. [8 points]



Since H of -OH end not observed + H_h signal overlaps with $H_f + H_g$ signals, use $H_a + H_b$ for chain end + $H_c + H_d + H_e$ for repeat units



$\Rightarrow 3(H_a + H_b) = 3.97$

$\Rightarrow$ CH_3 end groups $= 1.32$

$3(H_c + H_d + H_e) = 1.23 + 3.00 + 3.10 = 7.33$

$\Rightarrow$ CH_3 repeat units $= 2.44$

$\frac{\text{repeats}}{\text{ends}} = \frac{2.44}{1.32} = 1.85$

$\therefore$ primarily monomers + dimers

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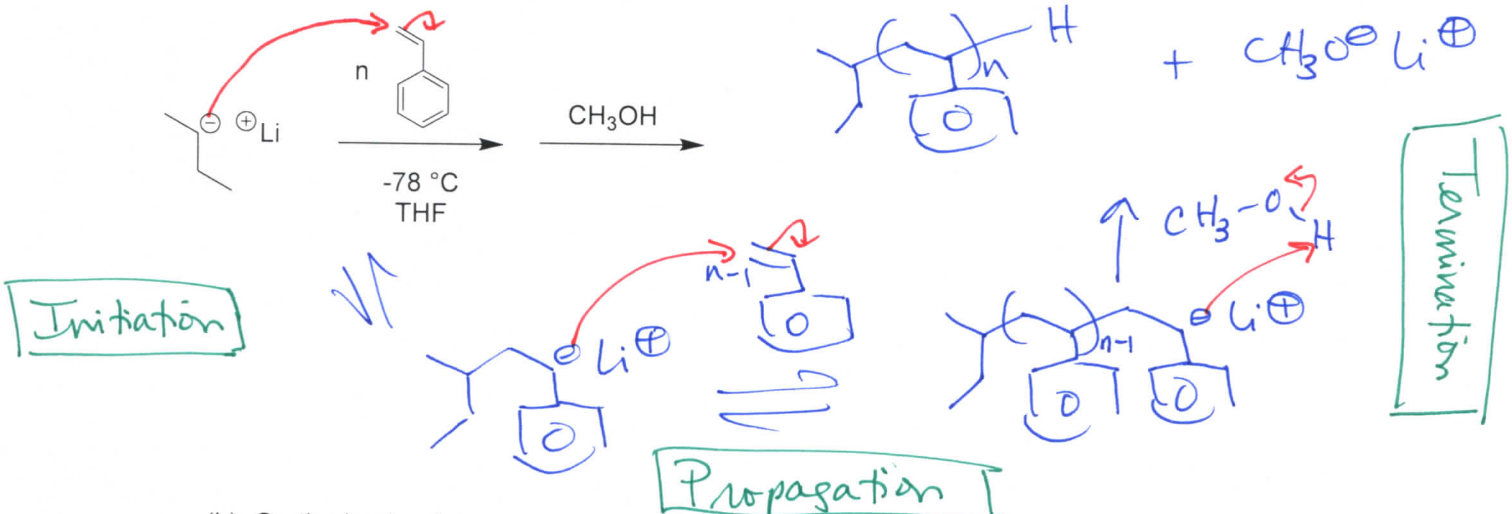
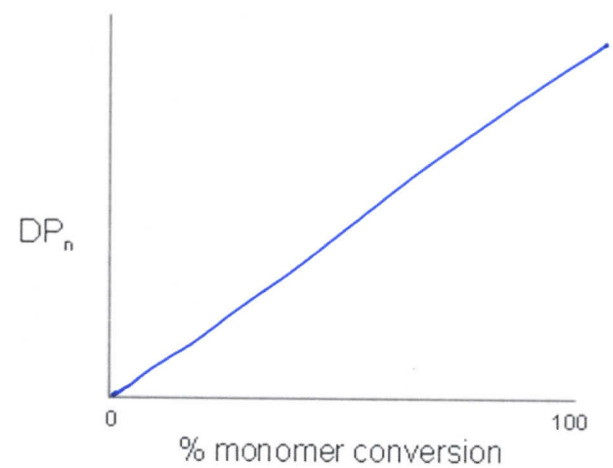
5. (a) Provide an electron arrow-pushing mechanism for the polymerization of styrene under the conditions given below, and give the final polymer structure. Label the initiation, propagation and termination steps. [10 points]



(b) On the basis of your assessment of whether this polymerization would ideally proceed as a step-growth or chain-growth polymerization and with or without control, draw the expected profile for DP_n vs. % monomer conversion on the axes below. [2 points]



(c) Given that ΔH = -73 kJ/mol and ΔS = -0.104 kJ/K·mol, would this polymerization be thermodynamically favorable at -78°C? Show your calculations. [4 points]

$-78\,°C = 195.15\ K$

$$\Delta G = \Delta H - T\Delta S$$

$$= -73\ kJ/mol - (195.15\ K)(-0.104\ kJ/K\cdot mol)$$

$$= -53\ kJ/mol$$

ΔG is -ve, ∴ polym is thermodynamically favored

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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 = 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:

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

Degree of branching:

$$DB = \frac{\#\text{ dendritic units} + \#\text{ chain ends}}{\#\text{ dendritic units} + \#\text{ chain ends} + \#\text{ linear units}}$$

Gibbs free energy change:

$$\Delta G = \Delta H - T\Delta S$$

Textbook:

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