Name: ANSWER KEY [printed]

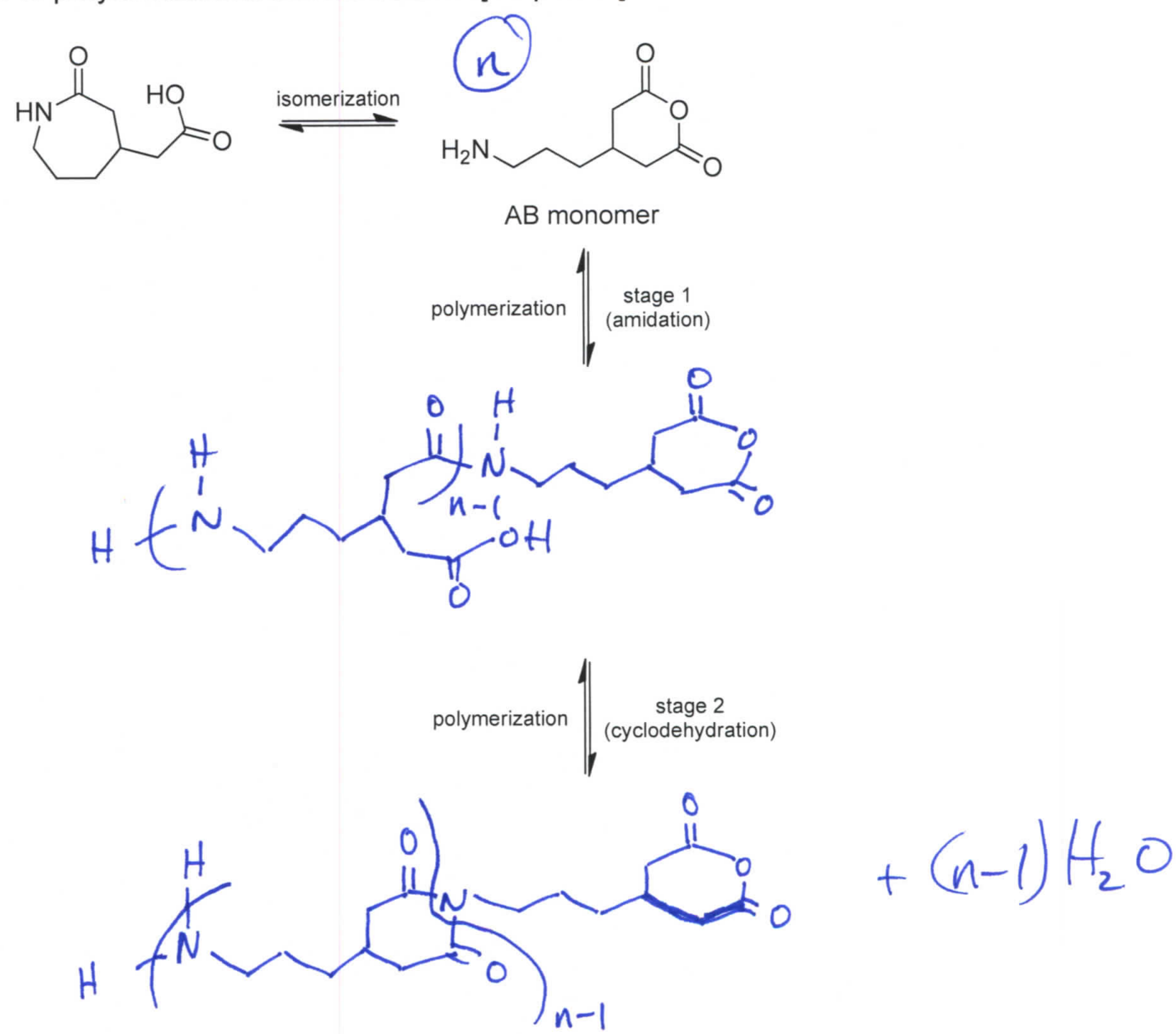
"On my honor, as an Aggie, I have neither given nor received unauthorized aid on this academic work."

______________________ [signature]

Exam II, February 24, 2011, 125 pts
Polymer Chemistry, CHEM 466, Spring 2011
Texas A&M University, College Station, TX, USA

1. As described in the textbook (Hiemenz, P. C.; Lodge, T. P. *Polymer Chemistry*, 2nd Edition; CRC Press, Taylor & Francis Group: Boca Raton, FL, USA, 2007) problem 2.3, heating of β-carboxymethyl caprolactam at 270 °C promotes isomerization to an AB monomer, which then undergoes polymerization to afford a polyimide.

   (a) Provide balanced chemical reaction equations that illustrate the chemical structures for the polymers and any condensation by-products for the two stages of polymerization shown below. [10 points]



it is difficult to draw the paranthuses, w/out exaggeration of the bonds

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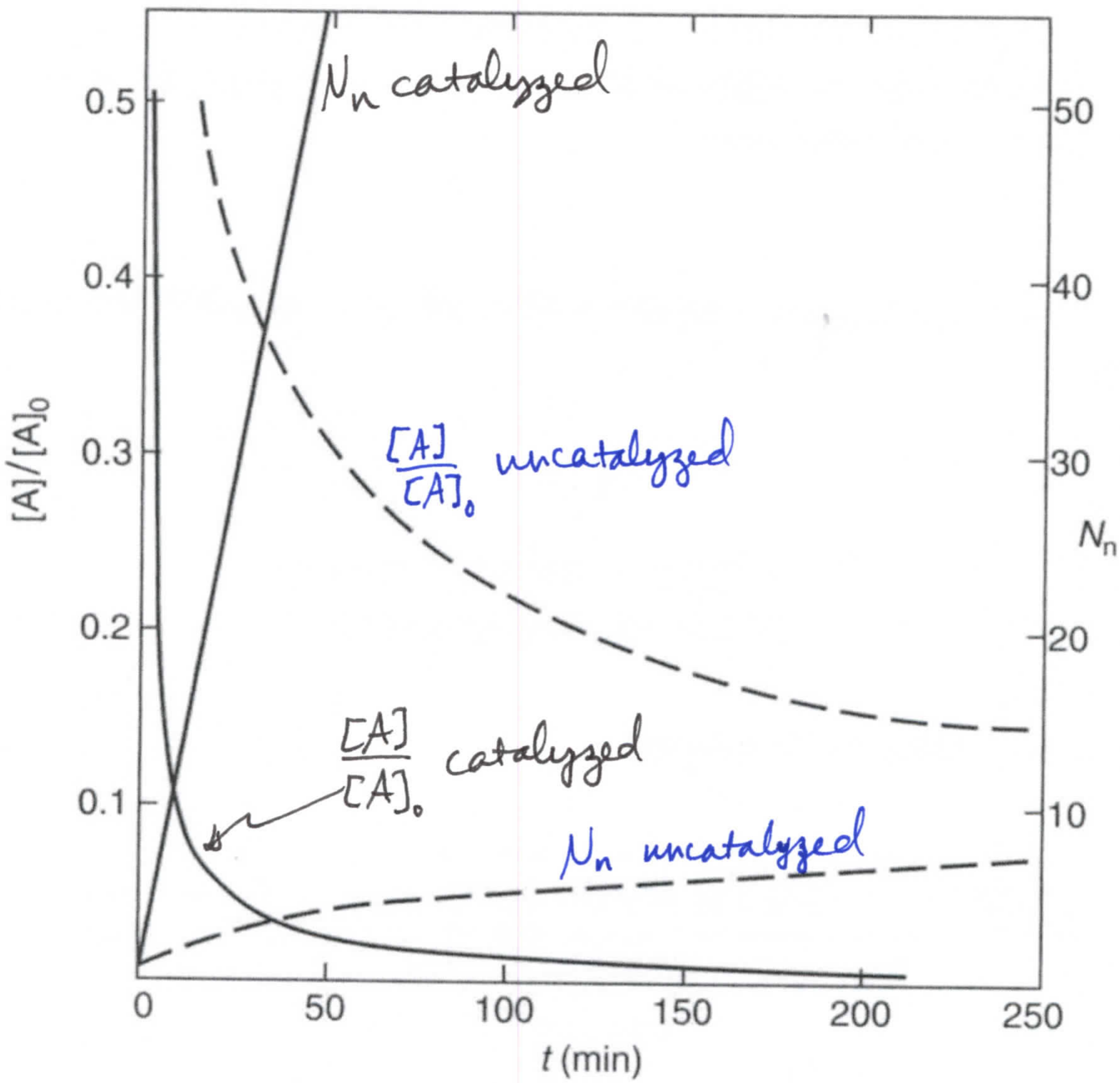
(b) Label the four plots of the figure below (Figure 2.4 of the textbook) to indicate which data are $[A]/[A]_0$ *vs*. time and N_n (also called DP_n) *vs*. time for a catalyzed AB polymerization reaction and which data are $[A]/[A]_0$ *vs*. time and N_n *vs*. time for an uncatalyzed AB polymerization reaction. [8 points]



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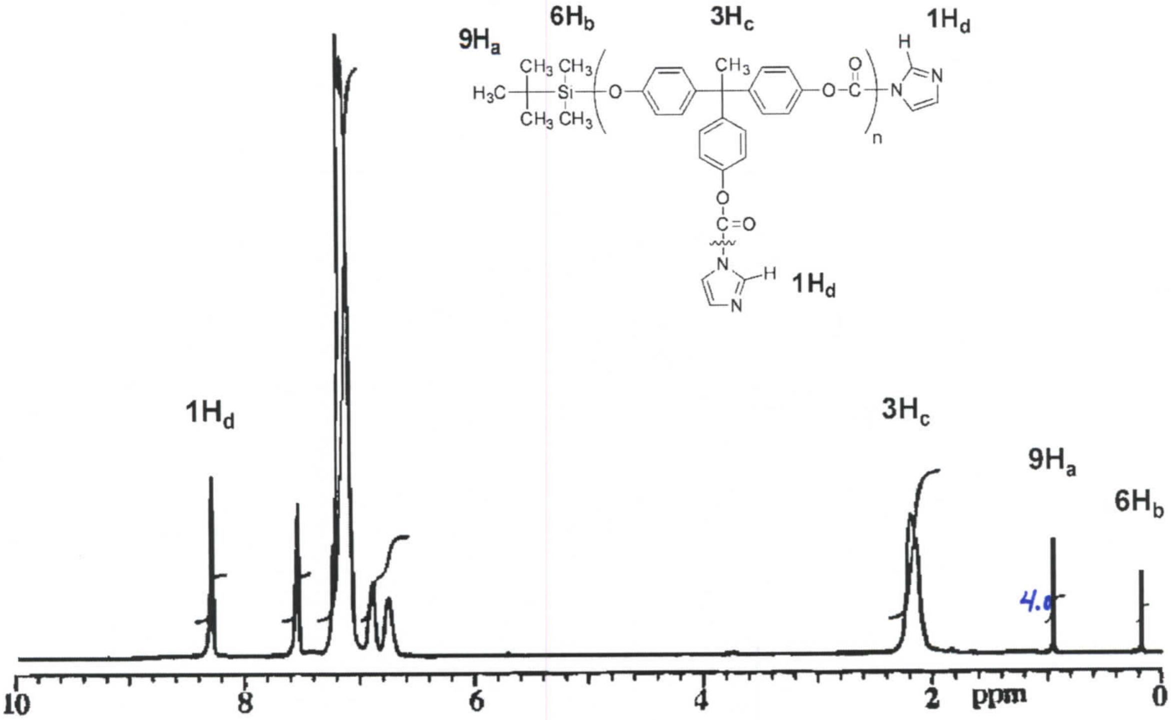
2. For the polycarbonate structure and ^1H NMR spectrum given:



[you can see that $3H_c$ is actually $(3n)H_c$ and $1H_d$ is actually $(1n+1)H_d$]

(a) Determine the degree of polymerization. [15 points]

use $9H_a$ or $6H_b$ for det'm of chain end relative #

for $9H_a$: $9H_a = 4.0\,mm \Rightarrow H_a = 0.44$

use $3H_c$ or $1H_d$ for det'm of repeat units (H_d complicated by 1 chain end too)

for $3H_c$: $3H_c = 19\,mm \Rightarrow H_c = 6.33$ $\quad \frac{H_c}{H_a} = 14.4 \Rightarrow DP_n = 14$

(b) Calculate the number-average molecular weight. [10 points]

repeat unit is $C_{25}H_{18}N_2O_5$; ignoring isotopic abundances,

repeat unit mass = 426 g/mol

chain ends are $C_6H_{15}Si$, mass = 115 g/mol

$C_3H_3N_2$, mass = 67 g/mol

$M_n = 14(426\ g/mol) + 115\ g/mol + 67\ g/mol$

$= 6146\ g/mol$

w/2 sig figs

$\Rightarrow$ 6100 g/mol

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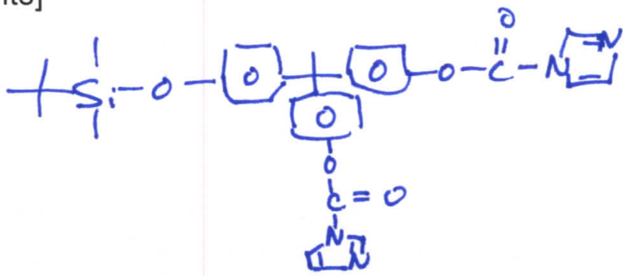
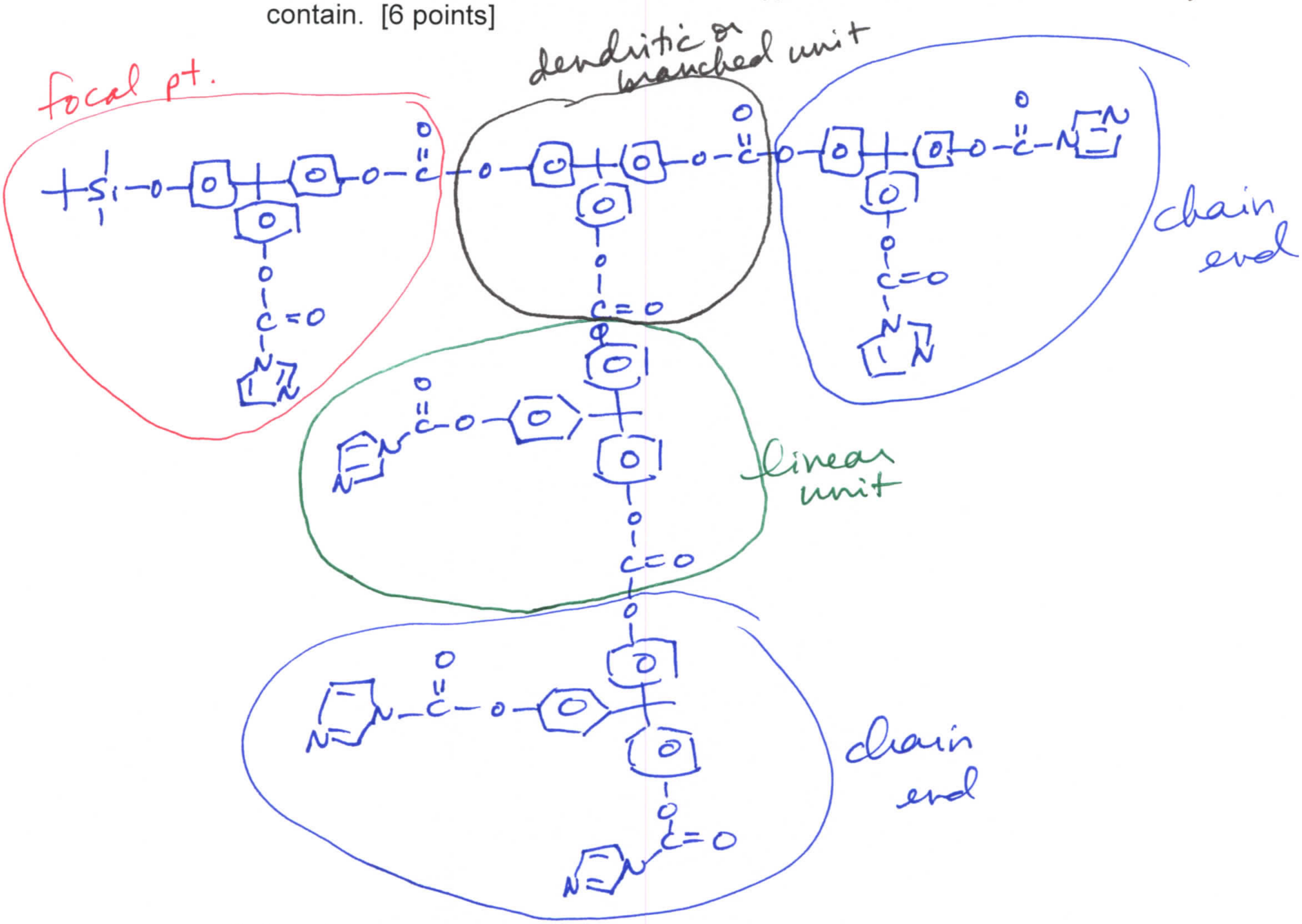
(c) Provide the structure for a monomer that could be used to produce this polymer. [5 points]



(d) Based upon your monomer and the wavy line included in the structure above, state the type of macromolecular architecture of this polycarbonate. [2 points]

hyperbranched polymer

(e) Draw-out the chemical structure, showing a sufficient number of repeat units to be able to illustrate the four different types of units that this structure may contain. [6 points]



(f) Label those different types of units upon your structure above. [4 points]

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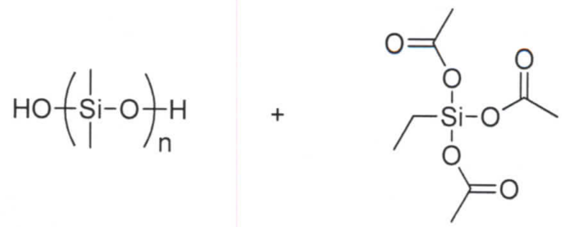
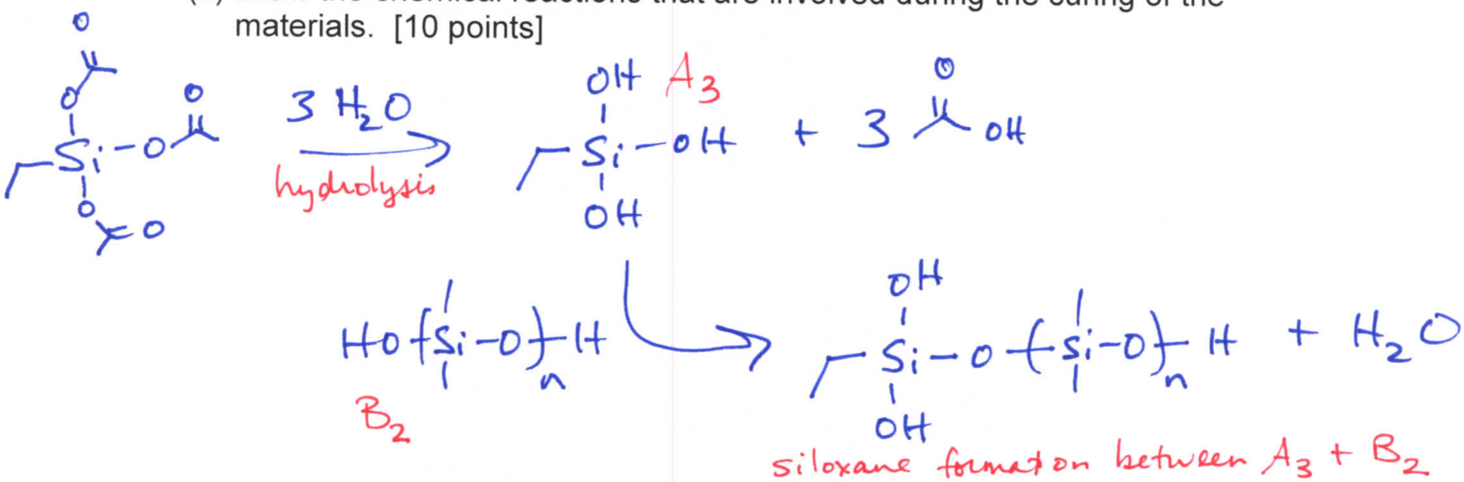
3. For the silicone adhesive components shown below:

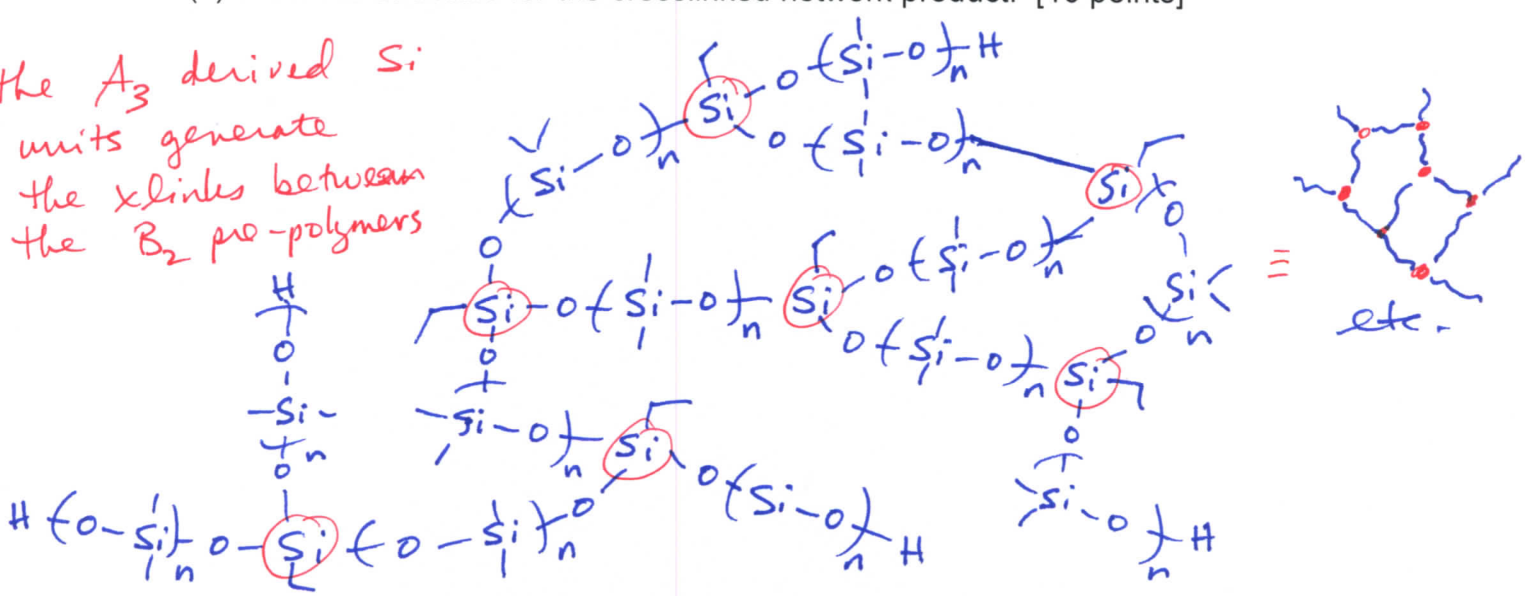


(a) Draw the chemical reactions that are involved during the curing of the materials. [10 points]



(b) Draw the structure for the crosslinked network product. [10 points]

the A_3 derived Si units generate the xlinks between the B_2 pre-polymers



(c) 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). [5 points]

for $A_3 + B_2$, stoichiometric balance requires $2\ A_3 + 3\ B_2$

$$\Rightarrow f_{av} = \frac{2 \cdot 3 + 3 \cdot 2}{2+3} = 2.4 \text{ and } P_c = \frac{2}{2.4} = 0.83 \Rightarrow 83\% \text{ gel pt.}$$

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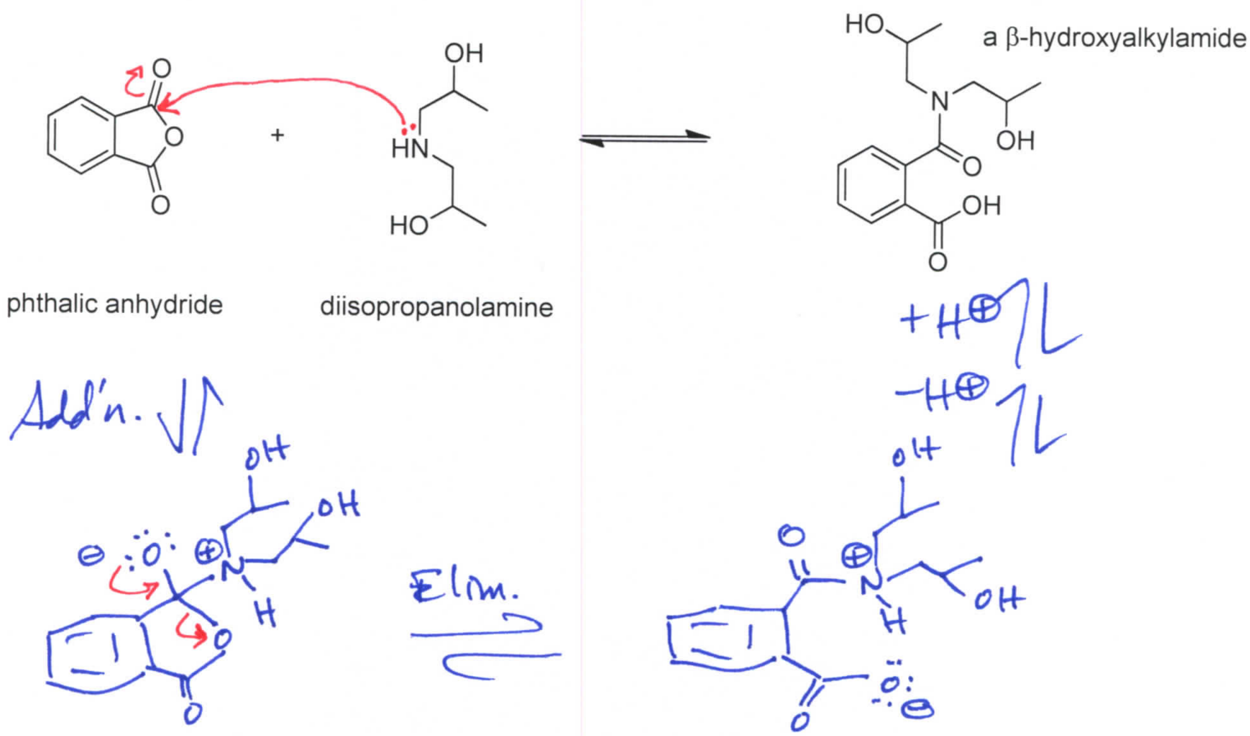
4. Provide detailed electron arrow-pushing mechanisms that allow for the establishment of the amide and ester linkages in DSM's Hybrane® polyesteramides.
   (a) Draw the mechanism for the reaction of phthalic anhydride with diisopropanolamine to give an initial β-hydroxyalkylamide. [6 points]



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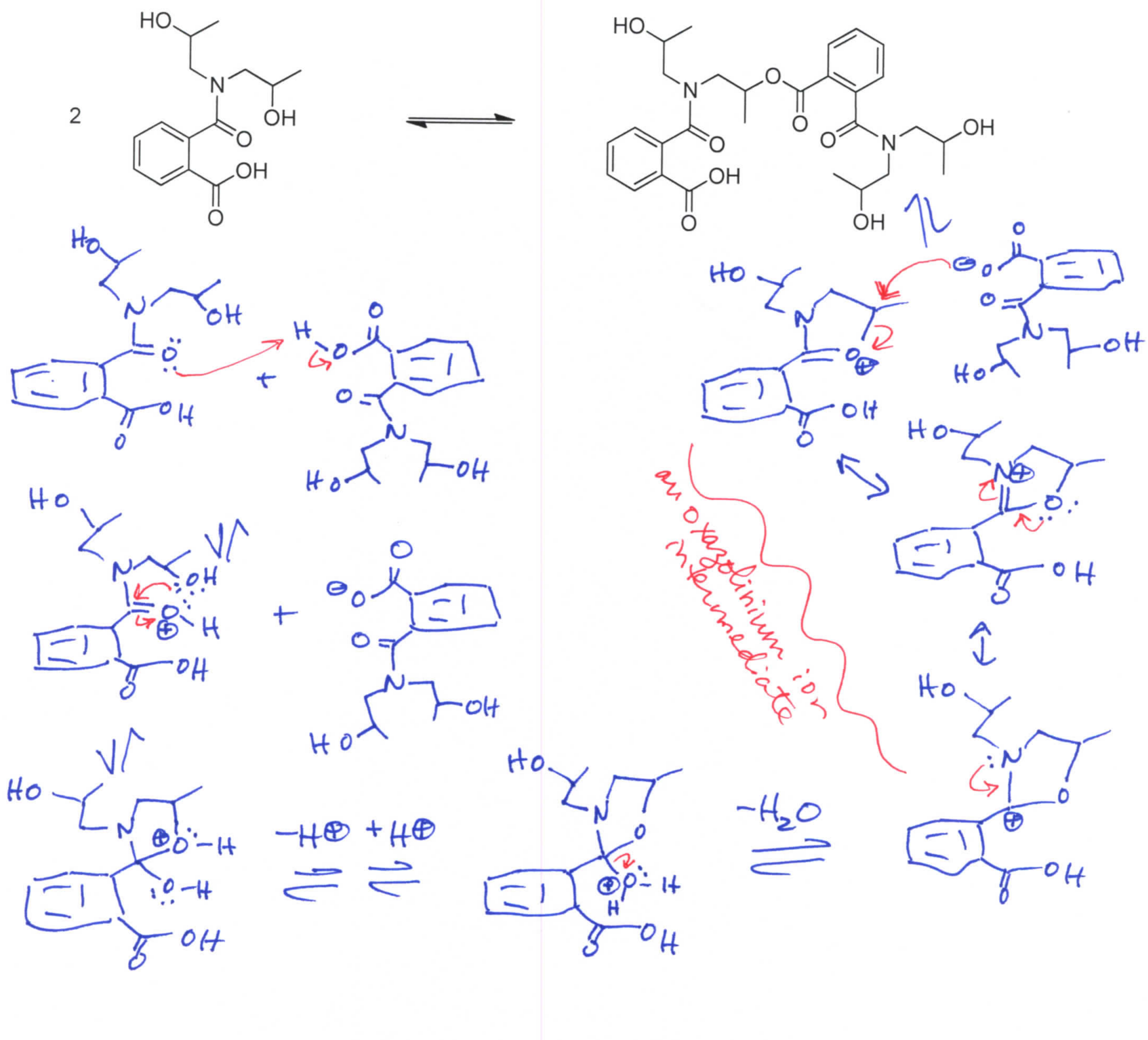
(b) Draw the mechanism for the reactions between two of the initial β-hydroxyalkylamides, which involve an oxazolinium ion intermediate, to give the esteramide structure shown. [10 points]



(c) Suggest two applications that may take advantage of the hyperbranched polymer architecture, and the unique physical and chemical properties that result. [4 points]

the article by P. Froehling, J. Polym. Sci., Part A: Polym. Chem. 2004, 42, 3110 - 3115 suggested several possibilities including polymer hosts for dyes + use as additives to polypropylene fibers, crystallization inhibitors for oil recovery, paper coatings, and others; also see J. Fréchet article from lecture.

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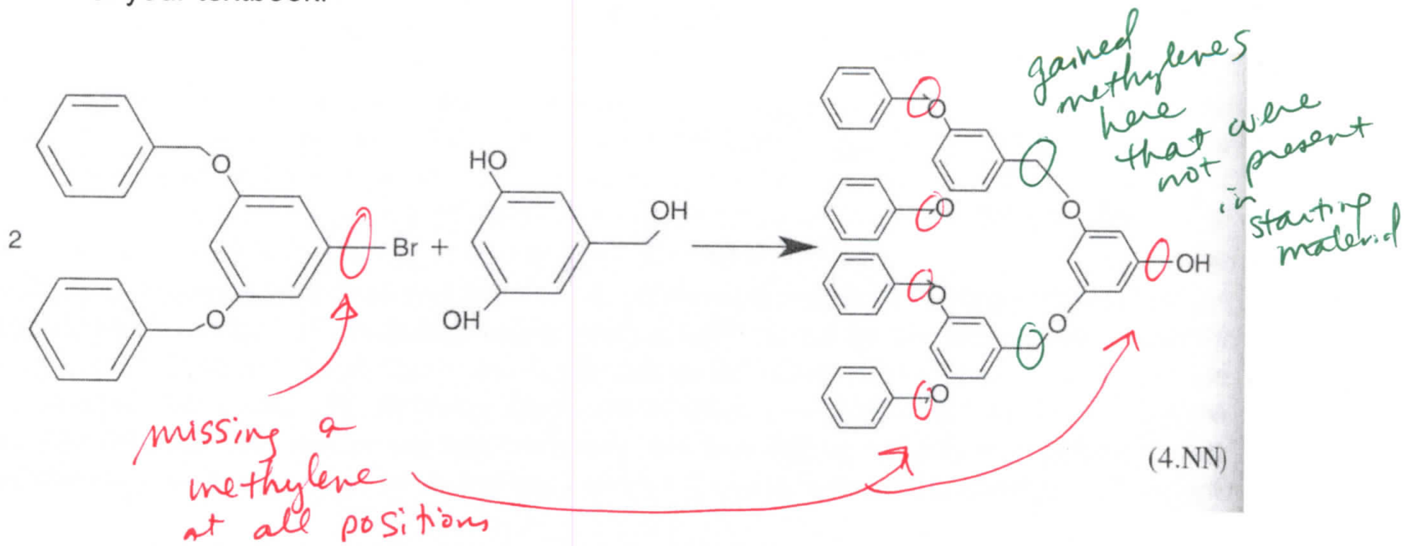
5. There are several errors in some of the chemical structures shown on page 160 of your textbook.



(4.NN)

(a) Identify the errors by circling them in the structures above. [5 points]

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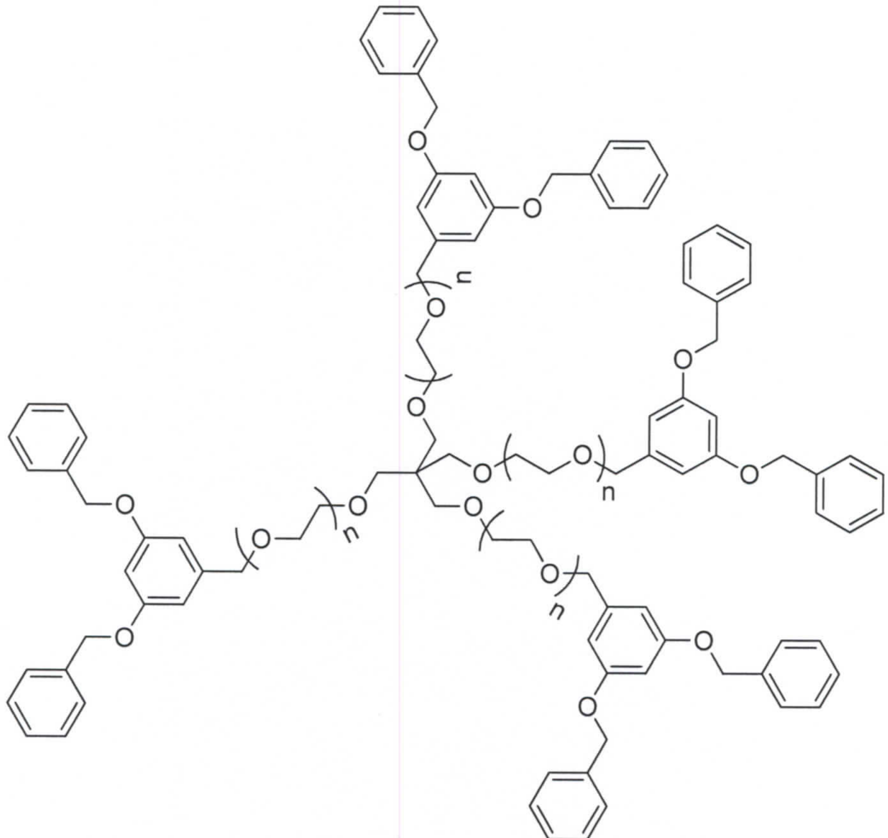
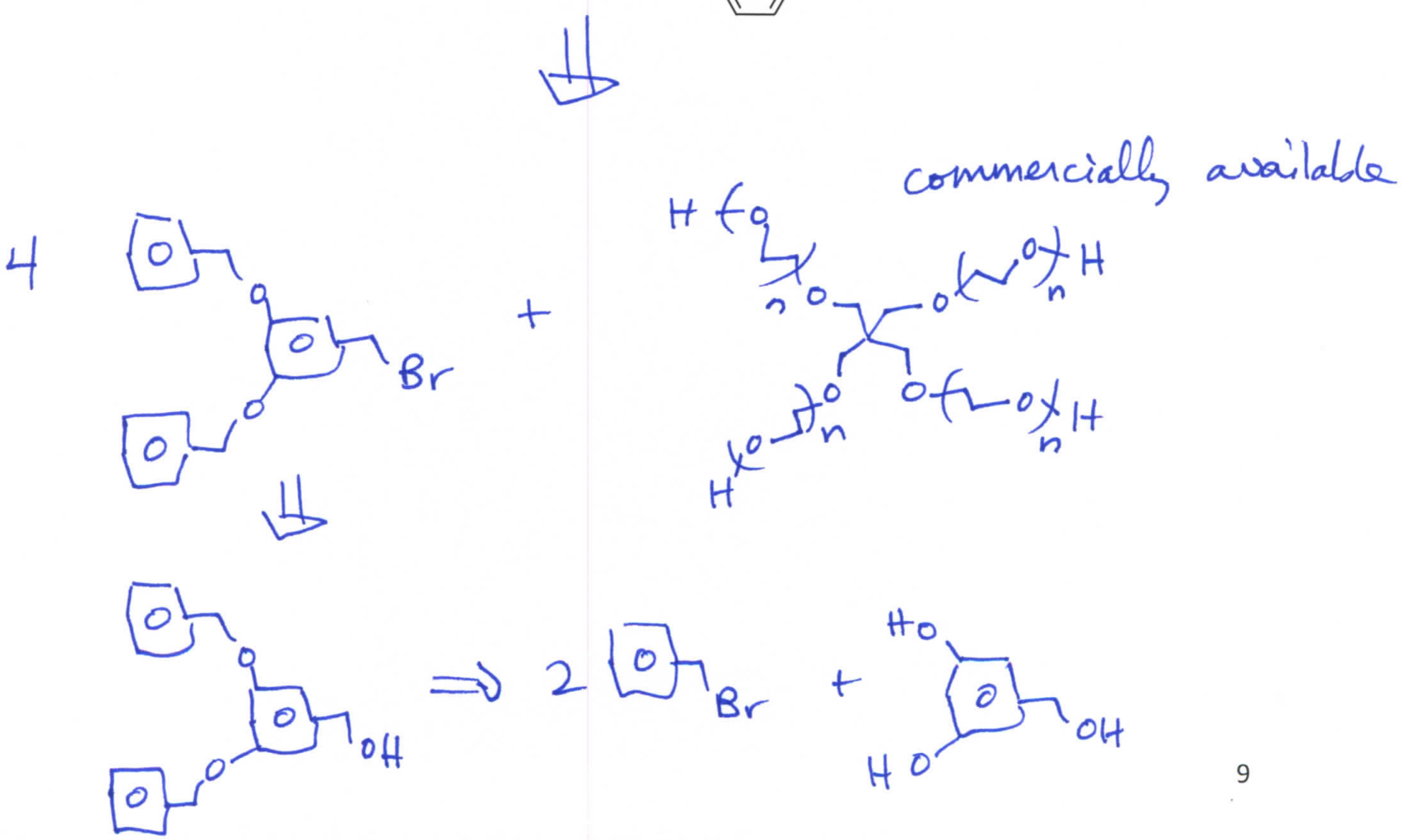
(b) Provide a retrosynthesis for the following hybrid dendritic-linear star polymer structure. [15 points]





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:

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

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

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