Name:_____[printed]

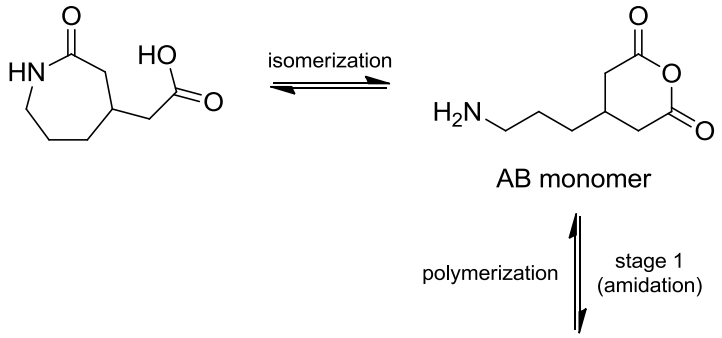
"On my honor, as an Aggie, I have neither given nor received unauthorized aid on this academic work."

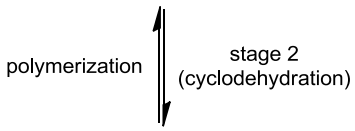
_____[signature]

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]





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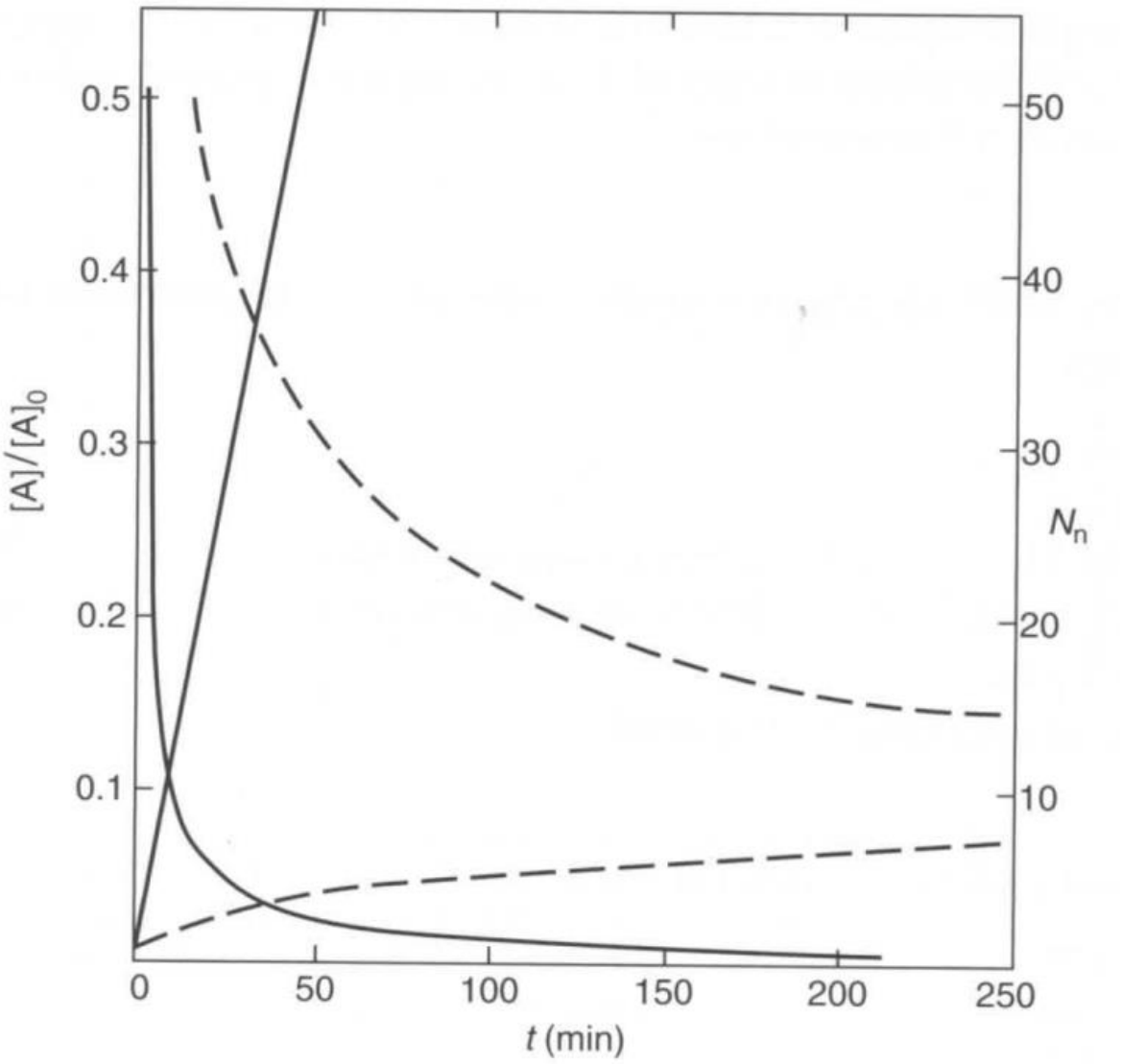
(b) Label the four plots of the figure below (Figure 2.4 of the textbook) to indicate which data are $[A]/[A]_0$ *vs*. time and N_n (also called DP_n) *vs*. time for a catalyzed AB polymerization reaction and which data are $[A]/[A]_0$ *vs*. time and N_n *vs*. time for an uncatalyzed AB polymerization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



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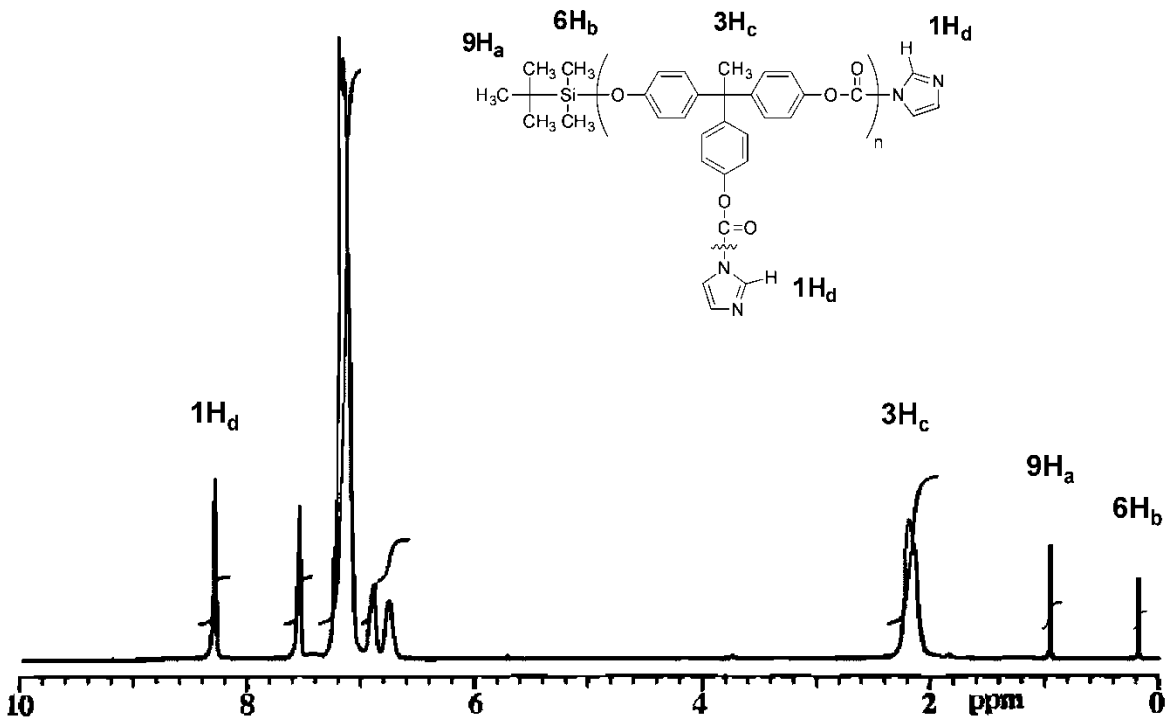
2. For the polycarbonate structure and ^{1}H NMR spectrum given:



[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]

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

(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]

(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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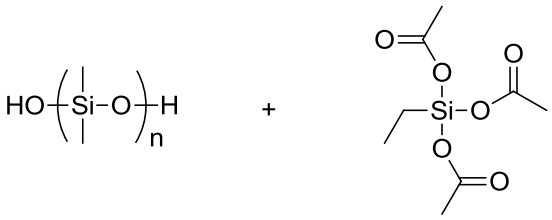
3. For the silicone adhesive components shown below:



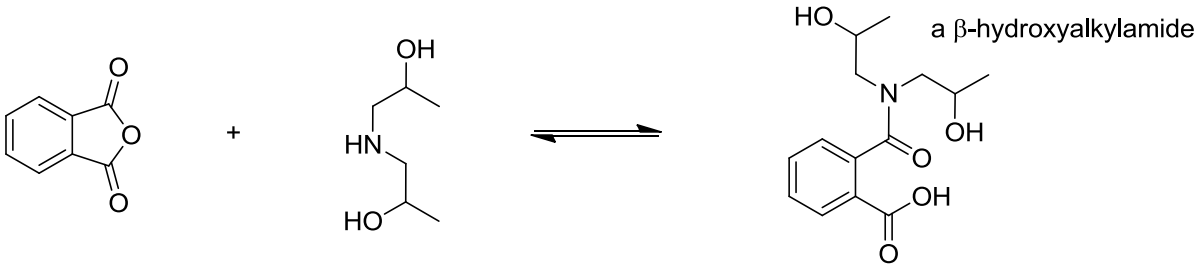
(a) Draw the chemical reactions that are involved during the curing of the materials. [10 points]

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

(c) Calculate the gel point (reminder: $p_c = 2/f_{av}$ and $f_{av} = \frac{\Sigma Nifi}{\Sigma Ni}$ for a stoichiometric balance of functional groups). [5 points]

Name:_____[printed]

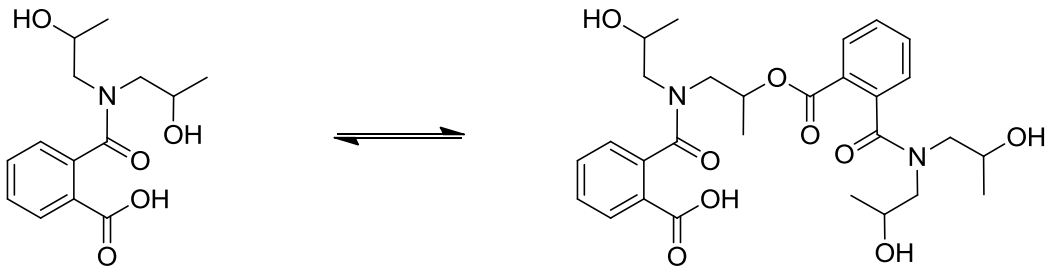
4. Provide detailed electron arrow-pushing mechanisms that allow for the establishment of the amide and ester linkages in DSM's Hybrane® polyesteramides.
   (a) Draw the mechanism for the reaction of phthalic anhydride with diisopropanolamine to give an initial β-hydroxyalkylamide. [6 points]



phthalic anhydride diisopropanolamine

(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]

2



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

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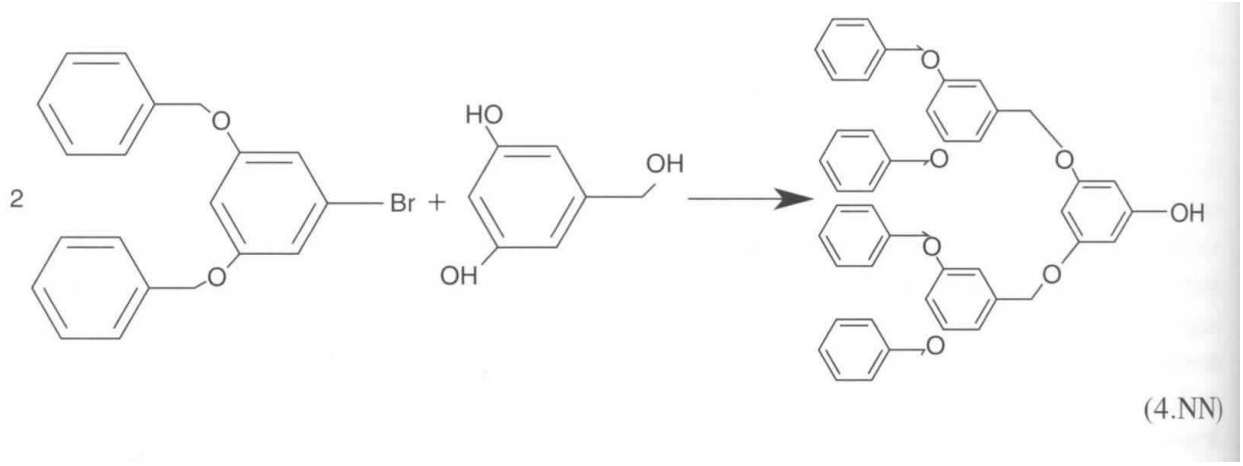
5. There are several errors in some of the chemical structures shown on page 160 of your textbook.



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

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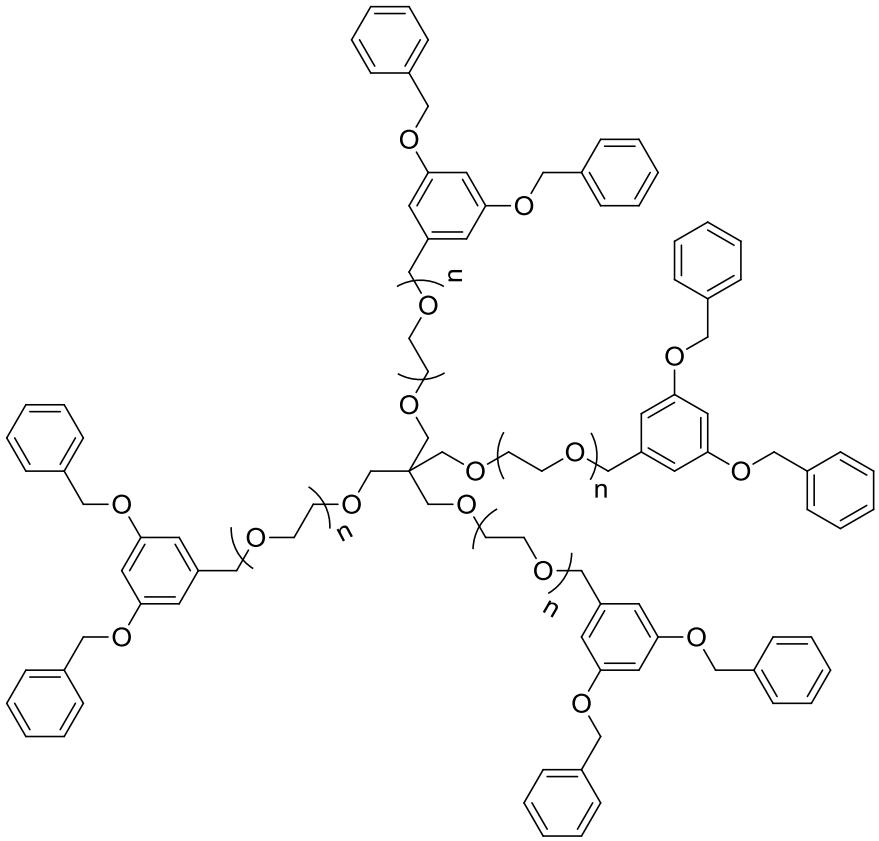
(b) Provide a retrosynthesis for the following hybrid dendritic-linear star polymer structure. [15 points]



Equations, which may be of use:

Number-average molecular weight:

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

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

Weight-average molecular weight:

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

$w_x =$ 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

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