Name:_____[printed]

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

_____[signature]

Exam III, March 27, 2012, 100 pts
Polymer Chemistry, CHEM 466, Spring 2012
**Texas A&M University, College Station, TX, USA**

1. If a polymer sample that has a fraction of insoluble material is dissolved into tetrahydrofuran for analysis by size exclusion chromatography (SEC), which requires a filtration process prior to injection into the SEC, what information would be needed to obtain an absolute weight-average molecular weight by light scattering detection and how would that information be obtained? [12 points]

2. (a) List four (4) key features of chain-growth, addition polymerizations. [8 points]

    1.

    2.

    3.

    4.

    (b) On the axes below, draw the typical plots for degree of polymerization vs. monomer conversion for: (i) a controlled chain-growth polymerization; (ii) an uncontrolled chain-growth polymerization; (iii) a step-growth polymerization. [10 points]

DP_n

0   % monomer conversion   100
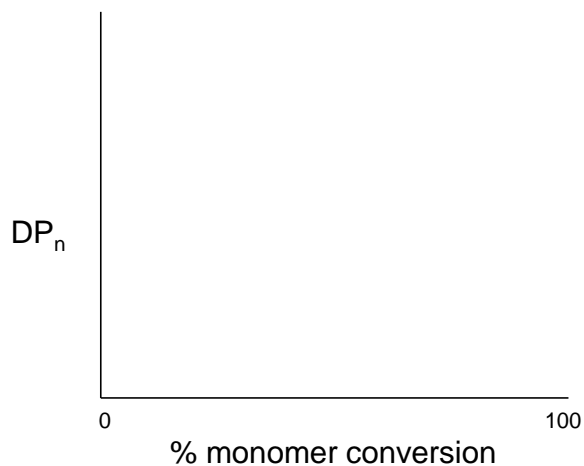
3. Polymer Factory (www.polymerfactory.com) is a Swedish company that provides a library of dendritic, hyperbranched and hybrid linear-dendritic polymer materials, including the structure shown below.

PFD-G3-PEG-OH
Number of -OH: 16
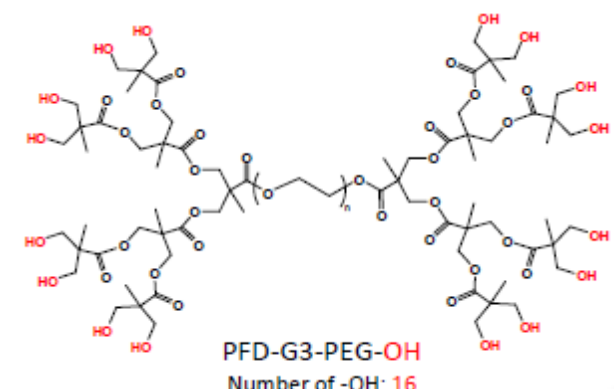
(a) From the ^{1}H NMR spectral data and the ^{1}H peak assignments to the structure, determine the degree of polymerization, n, of the poly(ethylene glycol)-derived linear core segment, and calculate the number-average molecular weight, M_n, for the entire macromolecule. Please note that you can choose to either measure the integrals with a ruler or use the integration values that are provided beneath the peaks (29.71, 20.28, 541.47, 18.30, and 24.00, respectively, from left to right, downfield to upfield resonance signals). [15 points]

CHCl$_3$

H$_2$O

7.26

4.29
3.81
3.78

1.93

1.29
1.07

29.71   20.28 541.47   18.30 24.00

f1 (ppm)
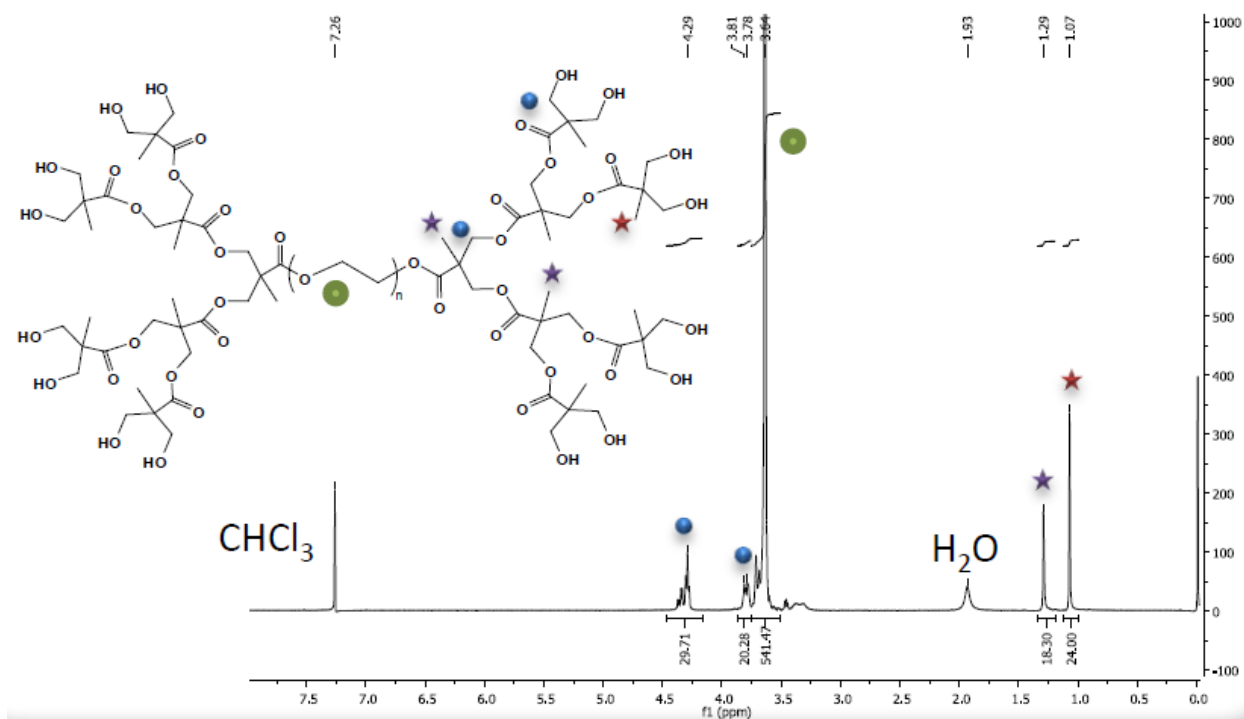
(b) The synthesis of the perfect dendritic-linear-dendritic hybrid structure of part (a) requires a stepwise approach with protection and deprotection reactions. However, an imperfect hyperbranched-linear-hyperbranched analog structure could be prepared more easily. Provide a retrosynthetic analysis for such a structure, working backwards to small molecules and showing the conditions that would be applied for the forward reaction sequence. [10 points]

Hyperbranched Polyester-Linear Poly(ethylene glycol)-Hyperbranched Polyester
Analog of the Dendritic-Linear-Dendritic structure shown above

⇓

4. For Yokozawa's chain-growth polycondensation to afford 4-arm star-shaped poly(*p*-benzamide)s discussed during lecture (Yoshino, K.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 6328-6332):
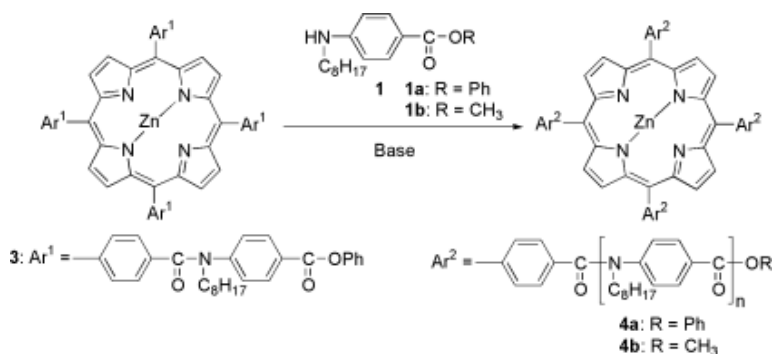

(a) Draw the chemical structures for the species that were observed in the three SEC peaks of the two SEC traces below, detected with absorption measurements at (A) 254 nm and (B) 430 nm. [15 points]
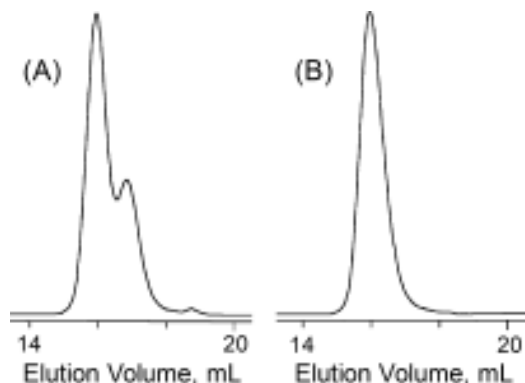
(b) Explain how the assignments of the structures to the SEC traces were made, *i.e.* state the characteristics of the structures and experimental conditions that allowed for confirmation. [5 points]

(c) Explain how the authors were able, in later experiments, to limit the production of the minority component observed at *ca.* 17 mL elution volume in SEC trace (A). [5 points]

4

5. The polycarbonate structure derived from the ring opening polymerization of a protected cyclic carbonate-based glucose monomer is shown together with two thermogravimetric analysis (TGA) traces obtained from two samples of the material, having slightly different degrees of polymerization. The initial temperature of thermal decomposition and the completeness of the thermal decomposition over a narrow temperature range are indicative of thermal degradation that breaks down the entire polymer chain into small molecules.
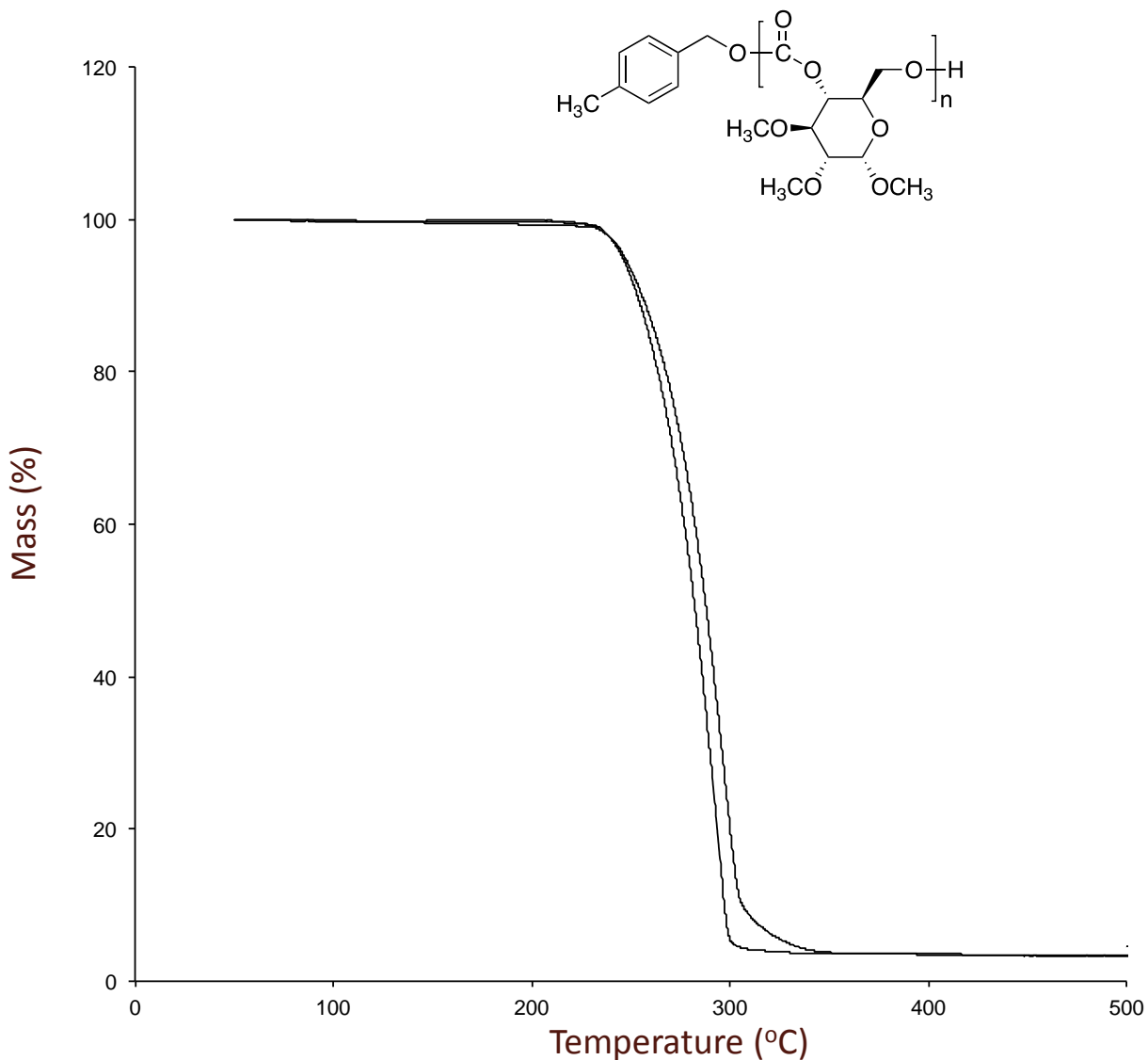
(a) Provide an electron arrow-pushing mechanism that could account for the thermal instability of this polycarbonate, and give the resulting products. [10 points]

(b) Diagram the primary components of a thermogravimetric analysis instrument. [10 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, $M_x = \dfrac{N_x M_x}{\Sigma N_x M_x}$

By light scattering, Zimm equation (eqn 8.5.18 of textbook)—
$$\frac{Kc}{R_\theta} = \frac{1}{M_w}\left(1 + \frac{q^2}{3}R_g^2 + \cdots\right) + 2Bc + \cdots$$

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

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