

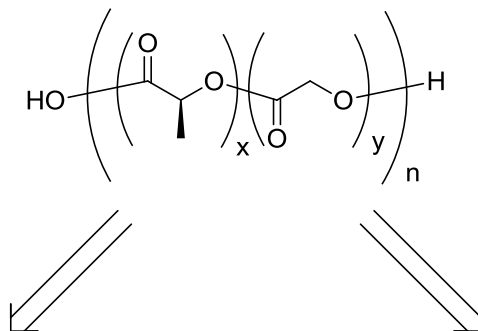
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“On my honor, as an Aggie, I have neither given nor received  
unauthorized aid on this academic work.”

\_\_\_\_\_ [signature]

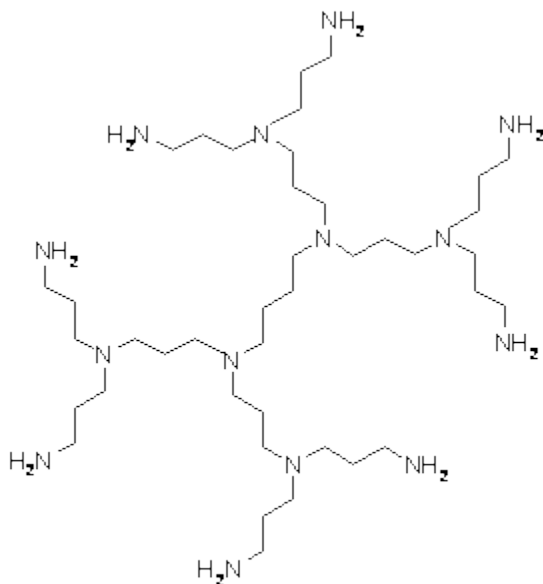
**Final Exam, May 7, 2012, 100 pts**  
**Polymer Chemistry, CHEM 466, Spring 2012**  
**Texas A&M University, College Station, TX, USA**

1. We discussed the use of poly(lactic acid) or polylactide in biomedical applications, such as in suture materials, and you've seen poly(glycolic acid) and polyglycolide on quiz #2. It is common for the properties of these two types of polyesters to be mixed, to obtain a polymer with intermediate crystallinity, hydrophobicity, mechanical properties and hydrolytic degradation rates, by the formation of copolymers that contain both types of repeat units along the polymer backbones. Consider only condensation, step-growth polymerization concepts, and reactions or side reactions that we have discussed for polyesters, to propose two quite different retrosynthetic routes that could be followed to give a mixed copolymer of lactic acid and glycolic acid repeat units. Work the retrosyntheses backward to the point that the forward syntheses begin from lactic acid and glycolic acid as the monomers, and provide the steps and reaction conditions that could be used to lead to the copolymer shown. Please note that your two approaches to this same copolymer structure may involve different numbers of steps. **[20 points]**



Name: \_\_\_\_\_ [printed]

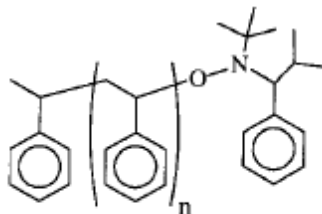
2. Provide a retrosynthetic route for the poly(propylene imine) dendrimer structure shown below (copied from <http://www.symo-chem.nl/dendrimer.htm>). [10 points]



Name: \_\_\_\_\_ [printed]

3. From the article Harth, E.; Hawker, C. J.; Fan, W.; Waymouth, R. M. *Macromolecules* **2001**, *34*, 3856-3862:

(a) Provide the starting materials and draw the forward sequence of electron arrow-pushing mechanistic steps for the preparation of the polystyrene structure, **12**, below. Be certain to label the initiation, propagation and (reversible) termination steps. **[10 points]**



**12**

Name: \_\_\_\_\_ [printed]

(b) What general type of polymerization is involved for the preparation of **12**, [2 points]

and what is the specific name for this particular sub-type of polymerization? [2 points]

(c) List four characteristics of this specific type of polymerization: [4 points]

(i)

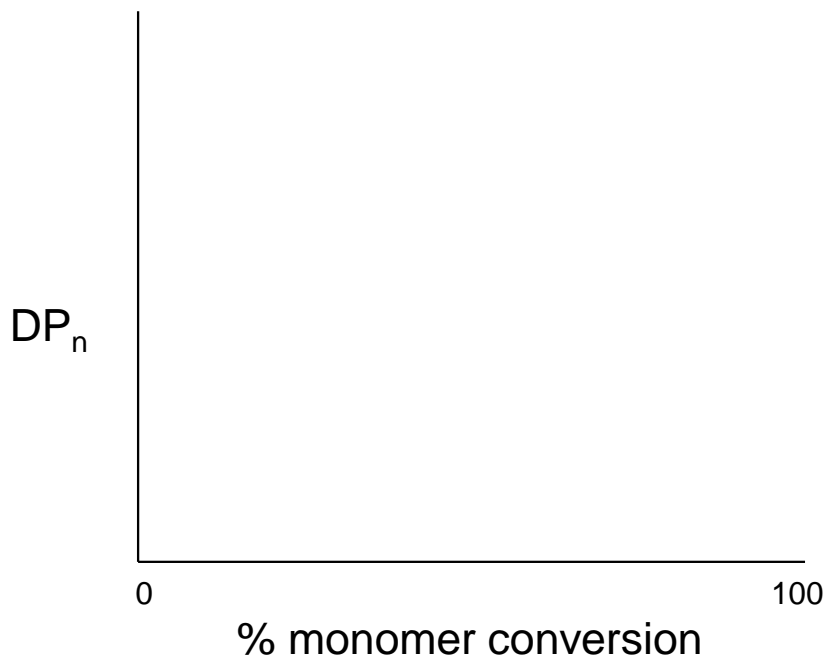
(ii)

(iii)

(iv)

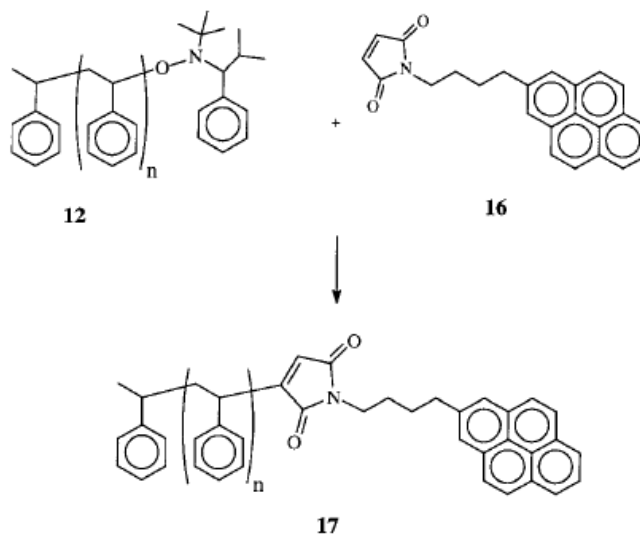
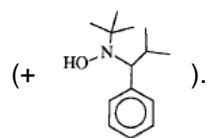
(d) Draw the typical  $DP_n$  vs. % monomer conversion plots on the axes below for: [6 points]

- (i) condensation, step-growth polymerization
- (ii) uncontrolled addition, chain-growth polymerization
- (iii) controlled addition, chain-growth polymerization

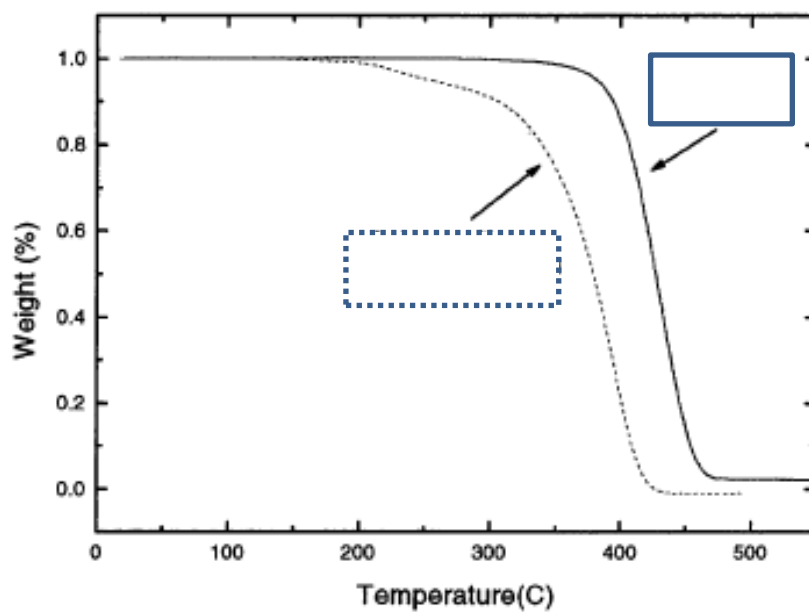


Name: \_\_\_\_\_ [printed]

- (e) Reaction of the alkoxyamino  $\omega$ -terminus of polystyrene, **12**, with a pyrene-substituted maleimide, **16**, afforded **17**



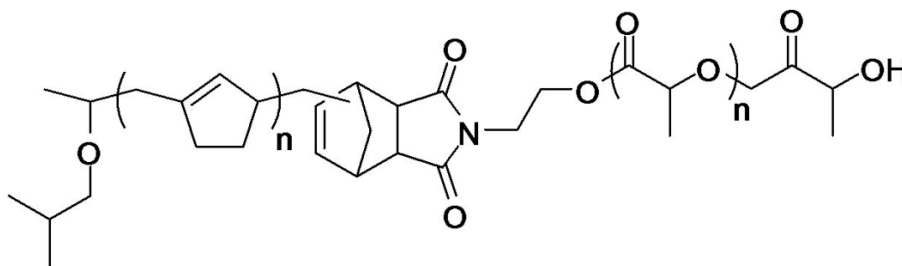
- (i) Within the two boxes associated with the thermogravimetric analysis (TGA) traces of the following figure, assign which of the polymers was responsible for the TGA data by writing its compound number, **12** or **17**. [2 points]



- (ii) Explain your answer to (i), in words and by showing the chemistry involved in the thermal degradation of the more thermally labile polymer. [4 points]

Name: \_\_\_\_\_ [printed]

4. Provide a retrosynthetic analysis for the block copolymer of the cyclic diene 3-methylenecyclopentene, 2, and lactide, as reported in Kobayashi, S.; Lu, C.; Hoyer, T. R. and Hillmyer, M. A. *J. Am. Chem. Soc.* **2009**, *131*, 7960-7961. [10 points]

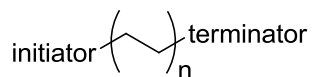
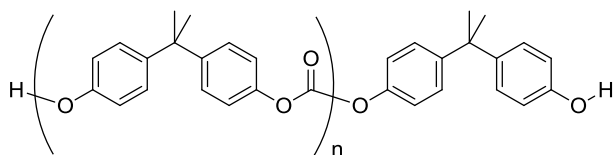
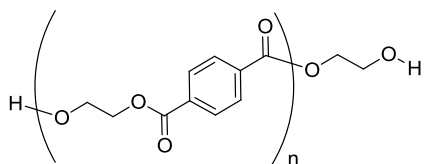


**poly-2-*b*-polylactide**

Name: \_\_\_\_\_ [printed]

5. (a) Evaluate and compare the following polymer structures to predict a ranking of their  $T_g$  values, with 1 being the highest and 3 being the lowest. **[3 points]**  
 (b) Provide brief explanations for your predictions. **[6 points]**  
 (c) State one product or application, in which each polymer is commonly employed. **[6 points]**

<u>Polymer Structure</u>	<u><math>T_g</math> ranking</u>	<u>Explanation</u>	<u>Typical product/application</u>
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(for the application, state whether it is for low or high degree of branching)

Name: \_\_\_\_\_ [printed]

6. Describe briefly the part of Professor Aida's lecture on April 17, 2012 that you found most interesting, in terms of the application, the characteristics or properties of the materials that provided performance in that application, and the composition and structure of the materials. **[15 points]**



**Equations, which may be of use:**

Number-average molecular weight:

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

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

Weight-average molecular weight:

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

$w_x$  = wt fraction of polymer chains having molecular weight,  $M_x = \frac{N_x M_x}{\sum N_x M_x}$

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:

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

**Textbook:**

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