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

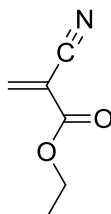
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Exam III, March 29, 2011, 125 pts
Polymer Chemistry, CHEM 466, Spring 2011
Texas A&M University, College Station, TX, USA

1. Superglue chemistry:

- (a) Explain *via* resonance structures why ethyl α -cyanoacrylate is capable of undergoing polymerization by initiation with water. **[10 points]**

ethyl α -cyanoacrylate

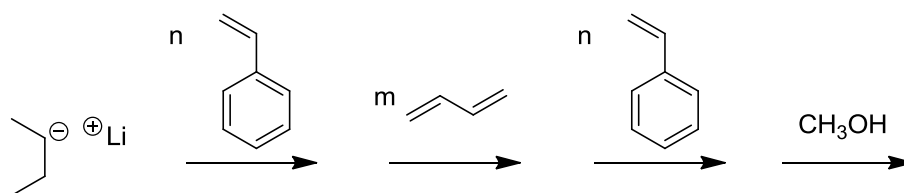


- (b) Draw the mechanisms involved with the water-initiated polymerization of ethyl α -cyanoacrylate, including any relevant resonance structures for intermediates. Label the steps of initiation, propagation and termination, and give the final polymer structure. **[20 points]**

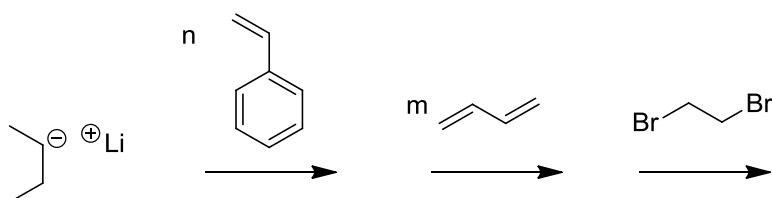
2. Polystyrene-*b*-polybutadiene-*b*-polystyrene triblock copolymers (abbreviated SBS, developed by Shell Oil Company and manufactured by Kraton Polymers) are high performance elastomers. They obtain their properties by phase separation of the polystyrene and polybutadiene components into nanoscopic domains, whereby the glassy polystyrene acts as physical crosslinks for the rubbery polybutadiene.

- (a) Polystyrene-*b*-polybutadiene-*b*-polystyrene can be synthesized either by sequential anionic polymerizations of styrene, butadiene and styrene followed by termination, or by sequential polymerizations of styrene and butadiene followed by coupling onto a bi-functional core. Draw the final structures that would result from each of those two techniques, represented by the following sequences of reactions (be certain to include all regiochemistries and stereochemistries for the butadiene repeat units, include brackets for the different block segments, parentheses for the copolymer segment, degrees of polymerization and chain ends): **[30 points (15 pts/each)]**

Sequential polymerization method



Coupling method



- (b) The polystyrene domains undergo a glass transition at ca. 100 °C, whereas the glass transition of polybutadiene occurs at ca. -90 °C. Therefore, over the wide temperature range from above -90 °C to below 100 °C, the material exhibits elastomeric properties, which allows use in extreme conditions and a broad range of applications. Differential scanning calorimetry (DSC) is a common method for measurement of glass transition temperatures. Diagram the components of a DSC instrument and provide the DSC trace that would be expected for a sample of polystyrene-*b*-polybutadiene-*b*-polystyrene. Label all of the components drawn for the DSC instrument, label the axes of the DSC trace, using actual temperature values and giving the direction of the endotherm, and label which transition belongs to which polymer. **[20 points (10 pts/each)]**

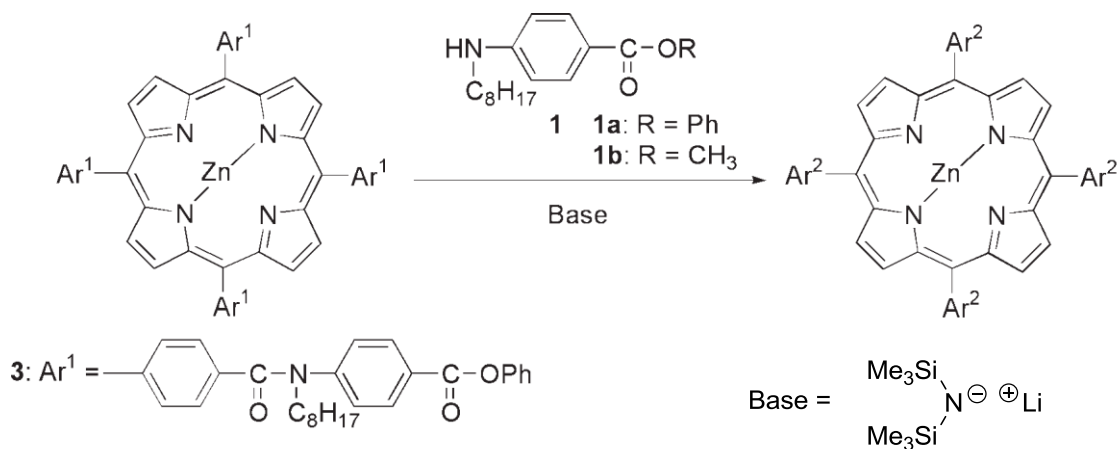
DSC instrument diagram

Expected DSC trace



3. 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):

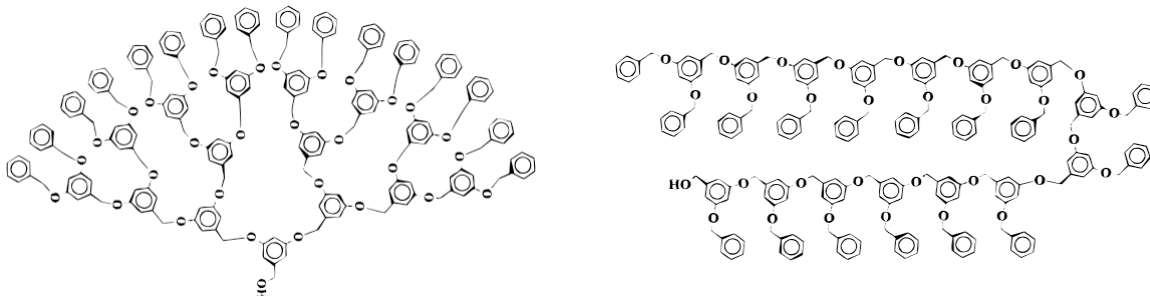
(a) Provide the electron arrow-pushing mechanisms for the deprotonation/activation of the monomer, initiation and propagation steps and give the final polymer structure (you need only to show the full chemical structure for one of the four arms and you can abbreviate the porphyrin core unit) for the polymerization of **1a** initiated by **3**, as illustrated in the scheme below. **[15 points]**



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- (b) List the four criteria that we discussed as being required to confirm living character for this polymerization (don't list only the measurement that would be made, but also what trait should be observed). **[8 points]**

4. Hawker *et al.* (Hawker, C. J.; Malmström, E. E.; Frank, C. W.; Kampf, J. P. *J. Am. Chem. Soc.* **1997**, *119*, 9903-9904) had demonstrated that dendritic macromolecules have a smaller hydrodynamic diameter than do their isomeric linear analogs, when of equivalent molecular weight, by using size exclusion chromatography (SEC, aka gel permeation chromatography, GPC).



- (a) Diagram the instrumental components that comprise a typical SEC system. Label each component, including at least one specific type of detector. **[7 points]**
- (b) Explain the mode of separation (*i.e.* how the column of a SEC functions) that allowed for detection of the hydrodynamic difference. **[5 points]**
- (c) Overlaid on one plot, draw the expected SEC traces for the dendrimer and linear polymer (include axes and axes labels). **[10 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

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*, 2nd Edition; CRC Press, Taylor & Francis Group: Boca Raton, FL, USA, 2007