Name:_____[printed]
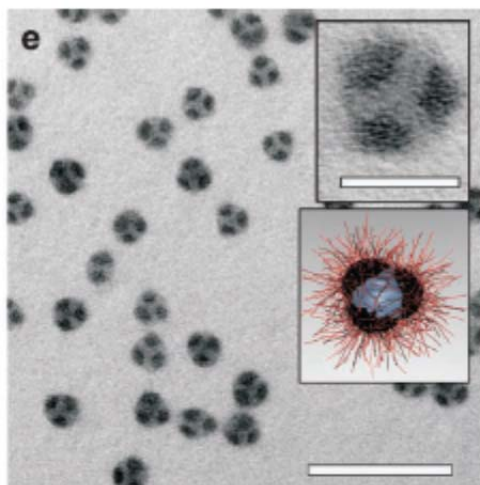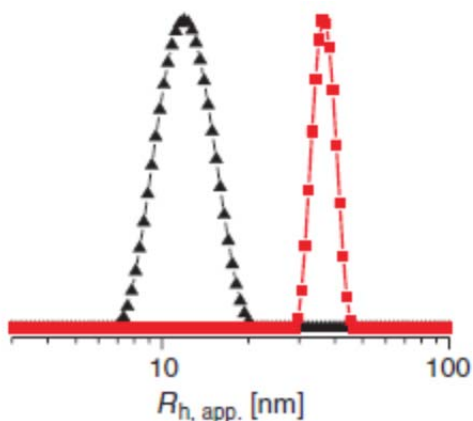
_____[signature]

Exam IV, April 24, 2012, 100 pts
Polymer Chemistry, CHEM 466, Spring 2012
Texas A&M University, College Station, TX, USA

1. (a) Provide a sequence of reactions that could be followed as a forward synthetic approach to prepare a polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate) triblock copolymer (PS_n-*b*-PB_m-*b*-$PMMA_p$) *via* anionic polymerizations, showing the product(s) formed at each step. This type of triblock copolymer was drawn in abbreviated form (as reproduced below) in the publication, Gröschel, A. H.; Schacher, F. H.; Schmalz, H.; Borisov, O. V.; Zhulina, E. B.; Walther, A.; Müller, A. H. E. *Nature Communications* **2012**, 3:710, DOI: 10.1038/ncomms1707, and it was shown to undergo assembly into multicompartment micellar nanostructures. Based on your forward synthetic route, draw the exact chemical structure of the polymer, being certain to illustrate the chain ends, any potential regiochemical and stereochemical variations, additives required, *etc.* **[10 points]**
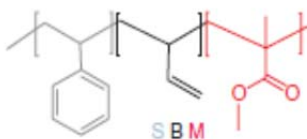
(b) The supramolecularly-assembled multicompartment nanostructure morphologies and dimensions were found to be dependent on the block copolymer chain lengths and the solvent systems employed.   For   instance,   when PS_{337}-*b*-PB_{333}-*b*-$PMMA_{369}$ was   transitioned   from N,N-dimethylacetamide (solvent for PS and PMMA, non-solvent for PB) to acetone/isopropanol mixtures (solvent for PMMA, non-solvent for PS and PB), 'clover' multicompartment micelles were produced. Explain the following dynamic light scattering data (each of the 2 plots) and transmission electron microscopy image (full scale bar = 200 nm, inset scale bar = 50 nm; staining was achieved with OsO_4), in terms of:

(i)   at which stage of the process they were acquired (*i.e.* with which solvent system) **[3 points]**
(ii) what type(s) of morphology(ies) are present, and **[3 points]**
(iii) where each polymer component resides within the nanoscopic morphology. **[3 points]**

2. For the butyl rubber tubing located on the table in the front of the classroom:
   (a) Draw the polymer structure. **[10 points]**

   (b) Provide a synthetic approach for its preparation, giving a sequence of forward reaction steps that include your choices for initiator(s), monomer(s) and terminator(s), based upon your chemical structure of part (a). **[5 points]**

   (c) Predict the favored regiochemistry and explain your prediction *via* comparison of the intermediates that lead to the possible repeat unit regiochemistries. **[10 points]**
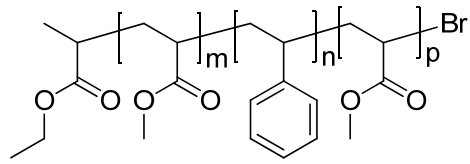
3. Provide retrosyntheses for the following poly(methyl acrylate)-*b*-polystyrene-*b*-poly(methyl acrylate) structures.

(a) **[10 points]**
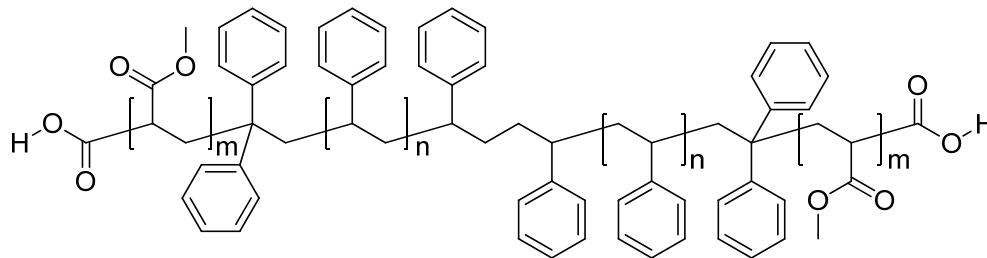
(b) **[6 points]**

4. For the low-density polyethylene (LDPE) packing material located on the table at the front of the classroom:

   (a) Draw the electron arrow-pushing mechanism for the azobisisobutyronitrile-initiated radical polymerization of ethylene, and label each of the initiation, propagation and termination (show only one type of termination, from the many possible reactions discussed) steps. **[10 points]**
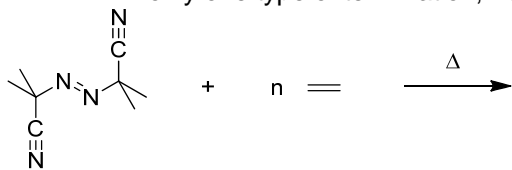
   (b) What is the predominant termination reaction that occurs and leads to the low density of LDPE? **[2 points]**

   (c) Provide an electron arrow-pushing mechanism for your answer to (b). **[8 points]**

5. During the anionic *vs.* cationic polymerization of the cyclic diene monomer, **2**, as reported by Kobayashi, S.; Lu, C.; Hoye, T. R.; and Hillmyer, M. A. *J. Am. Chem. Soc.* **2009**, *131*, 7960-7961:

  (a) Explain the conclusions that can be drawn from the ¹H NMR data of Figure 1, regarding the repeat unit regiochemical outcomes, as a function of the reaction conditions and the type of polymerization chemistry. **[10 points]**
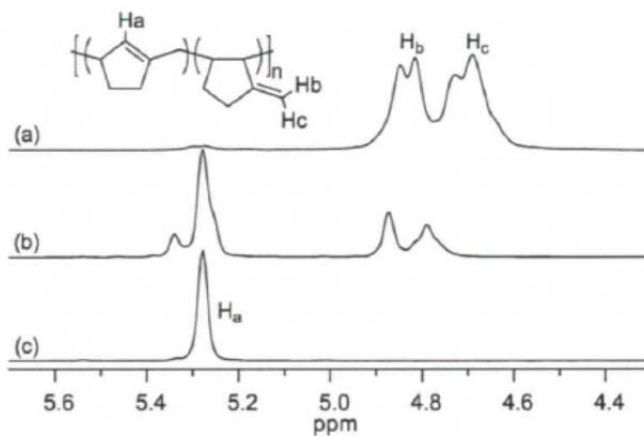

Figure 1. ¹H NMR spectra of poly-**2** prepared with (a) *s*-BuLi/TMEDA, (b) *s*-BuLi, and (c) *i*-BuOCH(Cl)Me/ZnCl₂/Et₂O.

(b) For the cationic polymerization conditions, use the general $R^+ X^-$ + monomer **2** reaction below, (redrawing it repeatedly, as many times as necessary), to show the electron arrow-pushing mechanism for addition reactions, giving all possible regiochemistries for the carbocation intermediates that could result. Compare their relative stabilities to explain the *ca.* 100% regiochemical control (*i.e.* explain why only one regioisomeric repeat unit was observed, and which one it is). **[10 points]**

$R^{\oplus}$ $^{\ominus}X$ +

2
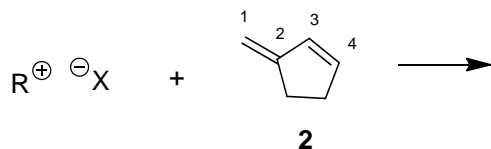
Equations, which may be of use:

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