

Part 1

Do Problem 7.1, 7.2, and 7.3.

Do Problem 8.2 and 8.3.

Do Problem 9.1, 9.2, and 9.4.

Do Problem 11.4.

Do Problem 13.1 and 13.2.

Do Problem 14.2.

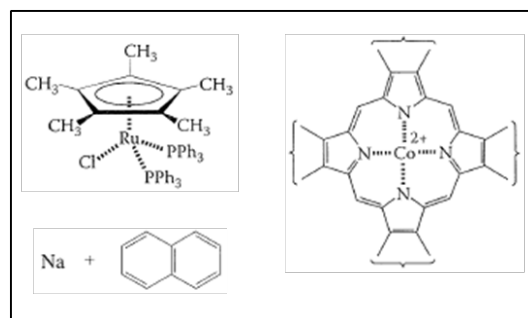
Part 2

1. Two monomers, X and Y, were copolymerized with styrene (ST), methyl acrylates (MA), and vinyl acetate (VAc). With the following monomer reactivity ratios found, answer the following questions.

A	B	r_A	r_B
X	ST	0.41	1.06
X	MA	0.76	0.09
X	VAc	3.4	0.07
Y	ST	0.02	2.3
Y	MA	0.14	4.4
Y	VAc	1.4	0.46

- (a) Are the copolymerizations radical, cationic, or anionic? Explain.
- (b) Which monomer pair could lead to azeotropic copolymerization? Explain.
- (c) Is ST monomer more reactive or less reactive than monomer X toward the X propagating center? By what factor?
- (d) List ST, MA, and VAc propagating center in the order of increasing reactivity toward monomer X.
- (e) When copolymerized with monomer X, which of ST, MA, or VAc will be incorporated in the copolymer chain with the smallest run number? [Run number is the number of times per 100 repeat units a copolymer chain switches from one type of comonomer unit to the other.]
- (f) Will monomer X or Y have the higher k_p in homopolymerization? Explain.
2. Answer the following questions.
- (a) [3 x 3 pts] In preparing block copolymers by living copolymerization, the order of monomer addition is critical. Describe the order in anionic, ATRP, and RAFT copolymerization.
- (b) [10 pts] There are four possible methods for the preparation of polybutadiene-*b*-polystyrene-*b*-polybutadiene (ABA triblock) copolymer via anionic living polymerization. What are they? No need to draw structure, just sketch and describe the methods. Beware of the copolymer sequence.
- (c) You want to prepare a poly(styrene-*g*-methyl methacrylate) with tapered distribution of the graft. Describe your synthetic steps with the catalyst or initiator you may use from the box on the right.

- (d) You want to prepare an alternating multi-block copolymer containing polystyrene and PET. Describe your synthetic steps with the catalyst or initiator you may use from the box on the right.



3. Answer the following questions.

- While membrane osmometry gives the number-average molar mass, light scattering method gives the weight-average molar mass. Explain.
- Dilute solution viscometry (DSV) gives only a 'relative' molar mass, not an absolute molar mass. Why is it regarded as 'relative'?
- Gel permeation chromatography (GPC) gives chromatogram as a function of elution volume, and the chromatogram is converted to one as a function of molar mass using 'universal calibration.' What is the observation that enables the calibration?
- DSV and GPC utilize an equation in common. Write down the equation. What is the name of the equation?