CHEM/CHM ENG C178 POLYMER SCIENCE AND TECHNOLOGY
Spring 2016, Midterm
March 15, 2016
80 minutes

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Read the direction carefully. All work must be done on exam pages. Show <u>all</u> work.

	Points	Out of
Problem 1		30
Problem 2		30
Problem 3		20
Problem 4		20
TOTAL		100

VIOLATING THE FOLLOWING WILL RESULT IN A ZERO ON YOUR EXAM.

- Accessing the internet is **NOT** allowed for the duration of the exam.
- ALLOWED:
    - Textbook: *Polymer Chemistry* by Hiemenz and Lodge
    - Your class notes
    - Your HW
    - Materials posted on bCourses
- NOT ALLOWED:
    - Computers and cellphones (turn them off and store them in a closed bag)
    - Other textbooks
    - Other classmates' HW
    - HW solutions from previous years
    - Exams from previous year

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Problem 1 Polymerization Approaches

(a) Estimate the molecular weight of a poly(butadiene) rubber tire that weighs approximately 8 kg. (5 pts)

(b) Draw a 10-mer of poly(propylene) polymerized using titanium tetrachloride $TiCl_4$ and triethylaluminum $Al(C_2H_5)_3$. (5 pts)

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(c) Zeigler-Natta catalysts often employ transition metal salts and an organometallic compound. Could n-butyllithium serve as the organometallic compound? Why or why not? (5 pts)

(d) Consider the copolymerization of styrene and butadiene by anionic synthesis. What is the mole fraction of styrene in a polymer made from a feed composed of 85% styrene with reactivity ratios $r_b = 14$ for butadiene and $r_s = 0.03$ for styrene. (5 pts)

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(e) An $\Delta G_m/kT$ vs. x_1 diagram is shown below. Label where the system is homogenous, show where it is phase separated. (5 pts)

(f) Approximate the radius of gyration R_g of a 10,000 g/mol poly(methyl methacrylate) molecule in acetone, a theta solvent, given that a 1,000 g/mol PMMA has a $R_g = 1.07$ nm. (5 pts)

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Problem 2 Step Growth Polymerization

Industrial synthesis of poly(dimethyl siloxane) (PDMS), a common silicone elastomer, is performed via the following pathway

$$n\,Si(CH_3)_2Cl_2 + n{+}1\,H_2O \rightarrow HO[-Si(CH_3)_2O-]_n\,H + 2n\,HCl$$

The monomer $Si(CH_3)_2Cl_2$ serves to stabilize eaction intermediates to catalyze the reaction. Consider the initial concentrations of monomers $[Si(CH_3)_2Cl_2]_0 = 0.2$ M and $[H_2O]_0 = 1$ M, and a reaction rate constant $k = 1 \times 10^{-3}\ s^{-1}$. Note that n is large so $n \approx n + 1$. The molar mass of the PDMS monomer unit $M_0 = 74$ g/mol.

(a) Derive an expression relating the concentration of $Si(CH_3)_2Cl_2$ to time, t, and the initial reactant concentrations $[Si(CH_3)_2Cl_2]_0$ and $[H_2O]_0$. You do not need to simplify the expression. (15 pts)

Useful integrals:

$$\int_{x_0} \frac{-dx}{x^2(y+x)} = \frac{x_0 - x}{x\,x_0 y} + \frac{1}{y^2}\log\left(\frac{x(x_0+y)}{x_0(x+y)}\right)$$

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(b) Derive an expression relating the number-averaged degree of polymerization to time, t, and the initial reactant concentrations $[Si(CH_3)_2Cl_2]_0$ and $[H_2O]_0$. You do not need to simplify the expression. (10 pts)

(c) How long would you have to run the reaction to produce a molecular weight M_n of 1000 g/mol? (5 pts)

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Problem 3 Chain Growth Polymerization

The manufacture of rubber used in commercial applications is a very precisely controlled process. Consider the radical polymerization of a 0.4 M solution of isoprene, $M_0 = 68\ \mathrm{g/mol}$, in tetrahydrofuran (THF) initiated by 0.003 M *2*-azobisisobutyronitrile. The reaction rate constants $fk_d = 1.3 \times 10^{-9}\ \mathrm{s}^{-1}$ and $k_p/k_t^{1/2} = 7.1 \times 10^{-2}\ \mathrm{L}^{1/2}\ \mathrm{mol}^{-1/2}\ s^{-1/2}$.

(a) Calculate the initial rates of initiation and propagation. (4 pts)

(b) Assuming no chain transfer, calculate the resulting molecular weight and dispersity of the initial polymer assuming termination by disproportionation. (8 pts)

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(c) In reality chain transfer occurs to both the monomer and to the solvent with chain transfer constants $C_M = 3 \times 10^{-5}$ for the monomer and $C_S = 5 \times 10^{-7}$ for the solvent. What is the change in molecular weight due to chain transfer? By how much did molecular weight decrease from (b)? (8 pts)

The density of THF $\rho = 889\ \mathrm{kg/m^3}$

The molar mass of THF $M = 72\mathrm{g/mol}$

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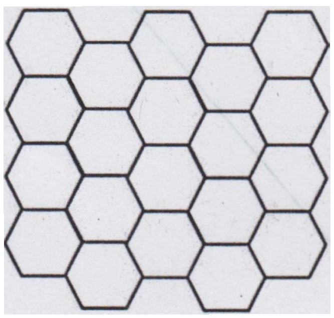
Problem 4 Solution Thermodynamics

We developed Flory-Huggins theory from a lattice model on which the pairwise interaction energies between the solvent (species 1) and the polymer segments (species 2) were unknowns w_{11}, w_{12}, and w_{22}. Consider the repeating lattice below containing 15% volume fraction of polymer with N=10 in a solvent. Each hexagon represents one lattice site.



(a) Calculate ΔS_m per lattice site from Flory-Huggins theory. (8 pts)

(b) Assuming $2w_{12} - w_{11} - w_{22}$ = kT/3.75, calculate ΔH_m per lattice site from Flory-Huggins theory. (8 pts)

(c) Will the polymer and solvent on this lattice be phase separated or homogenous? (4 pts)

Useful Constants:

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