Polymer Properties and Polymerization

CHEM 471 Midterm Exam

Professor: Jean Duhamel

Date: Wenesday February 28th, 2007

Duration: 1 hr 20

Material allowed: pen, ruler, calculator

Location: C2-361

Time: 1:30 – 2:50

Question #1: Copolymerization (70%)

1.1. Give the definition of the reactivity ratios r_1 and r_2 when the monomers M_1 and M_2 are copolymerized.

1.2. On the same graph, sketch a plot of f_1 vs. p and F_1 vs. p when the reactivity ratios r_1 and r_2 both equal 0.1 and the initial feed composition is such that $(f_1)_{t=0} = 0.7$. You will rationalize the trends you sketched based uniquely on the definition of the reactivity ratios.

1.3. Sketch the distribution of probability $(\underline{N}_1)_x$ and $(\underline{N}_2)_x$ of finding an uninterrupted sequence of x monomers M_1 and M_2 in the copolymer when $f_1 = f_2 = 0.5$, and $r_1 = 0.2$ and $r_2 = 5$.

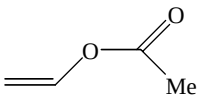
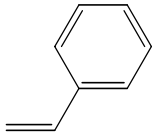
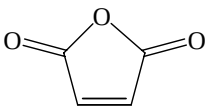
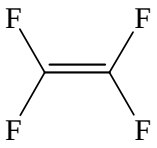
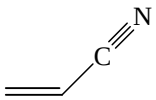
1.4. What is the *Q-e* scheme?

1.5. How would one use the *Q-e* scheme to answer the following questions?

a) Which monomer is vinyl acetate most likely to copolymerize efficiently with: styrene, maleic anhydride, or vinyl tetrafluoride? Explain why and what type of copolymerization would result.

b) Would an efficient copolymerization occur between acrylonitrile and styrene. Explain why and what type of copolymerization would take place.

Table 1: Names and chemical structures of monomers.

				
Vinyl acetate	Styrene	Maleic anhydride	Vinyl tetrafluoride	acrylonitrile

Question #2: Ionic polymerization (30%)

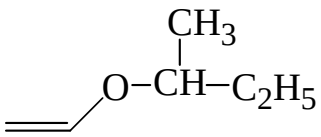
2.1. $SbCl_5$, trityl chloride ($(C_6H_5)_3CCl$), and isobutyl vinyl ether (*i*BVE) are mixed in dichloromethane (CH_2Cl_2). Explain what type of polymerization occurs and how it happens? Could it have happened if styrene had been used instead of *i*BVE?

2.2. Using the data listed in Table 1, determine the expected number average degree of polymerization (X_n) of poly(*i*BVE) when [*i*BVE] equals 0.5 M.

2.3. Sodium ([Na] = 10^{-5} M), naphthalene ([Np] = 10^{-5} M), and styrene ([Sty] = 10^{-1} M, MW = 104 g.mol^{-1}) are placed in 10 mL of THF and kept for 24 hours at –70 ^{o}C. The polymerization is living and it is terminated by adding a small amount of water. What is the molecular weight of the polystyrene at the end of the polymerization. You will explain your rational.

Table 2: Kinetic parameters for the polymerization of *i*BVE in dichloromethane at 0 °C.

Parameter	Value
$[(C_6H_5)_3CCl] = [SbCl_5]$	6.0×10^{-5} M
k_i	5.4 $M^{-1}.s^{-1}$
k_p^+	7.0×10^3 $M^{-1}.s^{-1}$
$k_{tr,M}$	1.9×10^2 $M^{-1}.s^{-1}$
$k_{ts} + k_t$	0.2 s^{-1}



isobutyl vinyl ether