

Problem Set 3

Answer Key

- $X_n = p[M]_0/[I]_0 = 0.72(5.0)/0.05 = 72$
 The molecular weight is $72 \times 104 = 7488$, which is close to the experimental value.
- An alkoxyamine and styrene are reacted to about 90% conversion and then 4-vinylpyridine is added.
- The components in emulsion polymerization are monomer, dispersing medium, emulsifier, and initiator. Emulsion polymerization has advantages similar to those of solution polymerization—easier thermal and viscosity control compared to bulk polymerization. The presence of dispersing medium is a disadvantage if one desires the product to be pure polymer. On the other hand, this is an advantage if one desires a polymer emulsion as the final product.

$$4. \frac{(R_p)_{\text{Bulk}}}{(R_p)_{\text{Emulsion}}} = (k_p[M](R_i/2k_t)^{1/2})/(10^3 N n k_p[M]/N_A) = [(R_i/2k_t)^{1/2} N_A] / 10^3 N n$$

$$= \{[(5.0 \times 10^{12} \times 10^3)/(6.022 \times 10^{23} \times 2 \times 6.0 \times 10^7)]^{1/2} (6.022 \times 10^{23})\} / (10^3 [1.0 \times 10^{15}] 0.5) = 1.0 \times 10^{-2}$$

$$(X_n)_{\text{Bulk}} / (X_n)_{\text{Emulsion}} = [2k_p[M] / (2R_i k_t)^{1/2}] / [N k_p[M] / R_i] = [2(R_i/k_t)^{1/2}] / N$$

$$= 1.0 \times 10^{-2}$$

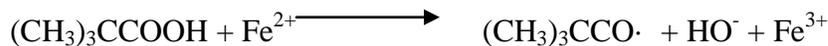
In both calculations it is necessary to make the needed conversions to express N and R_i into units of mol L^{-1} and $\text{mol L}^{-1} \text{s}^{-1}$, respectively.

The emulsion polymerization proceeds with a rate 100 times faster than the bulk polymerization and yields a polymer whose molecular weight is 100 times larger. Note that the molecular weight calculation assumes the absence of chain transfer.

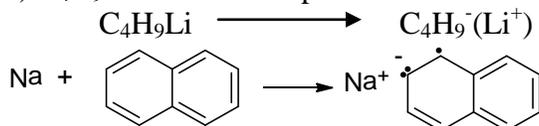
The separate control of rate and molecular weight in bulk or other homogeneous polymerizations is very limited. Changing the initiation rates affects the rate and molecular weight in opposite directions. For example, increasing the concentration of initiator or using more reactive initiator results in higher polymerization rate, but lower polymer molecular weight. The effect of temperature varies with the type of initiation. Higher temperature increases rate but lowers molecular weight when initiation occurs by thermal decomposition of an initiator such as AIBN or peroxide. Redox polymerization proceeds with small increases in rate and molecular weight with increasing temperature.

For emulsion polymerization, increasing N results in increases in both polymerization rate and polymer molecular weight. One can vary the rate without affecting molecular weight by varying N while keeping N/R_i constant. Alternately, molecular weight can be varied at constant polymerization rate by varying N/R_i at constant N .

- a) $(\Phi\text{COO})_2$ and $(\text{CH}_3)_3\text{COOH} + \text{Fe}^{2+}$ are radical initiators:



b) $\text{C}_4\text{H}_9\text{Li}$ and $\text{Na} + \text{Naphthalene}$ are anionic initiators:



c) H_2SO_4 and BF_3 are cationic initiators. The initiating species are H^+ in both systems. The proton donor in the second system is the complex formed from the two components BF_3 and H_2O .

d) Lower temperature and moderately polar solvents are generally required for ionic polymerizations, compared to radical polymerizations.

e) All of the monomers except isobutylene, n-butyl vinyl ether, and formaldehyde are polymerized by radical initiators. The radical polymerization of thiocarbonyl fluoride requires low temperatures. Cationic polymerization occurs with isobutylene, styrene, n-butyl vinyl ether, and formaldehyde. Anionic polymerization occurs with styrene, vinylidene cyanide, methyl methacrylate, formaldehyde, and thiocarbonyl fluoride.

6. The experimental observations could be consistent with either a radical chain, anionic chain, cationic chain, or step mechanism.

a) Most, but not all, chain polymerizations proceed with the polymer molecular weight decreasing as temperature increases. The exceptions are photochemical and redox radical polymerizations and some cationic polymerizations. The effect of increasing temperature on polymer molecular weight for step polymerization is variable. Increasing temperature can increase polymer molecular weight by making it easier to displace the equilibrium toward polymer expulsion of the small molecule by-product. Alternately, higher temperature can decrease the polymer molecular weight by displacing the equilibrium to the left.

b) The polymer molecular weight can vary with solvent for any polymerization. The polymer molecular weight for a radical polymerization can vary with solvent because one solvent is a stronger chain transfer agent than the other solvent. The rate and degree of polymerization of ionic chain polymerizations are affected by solvent polarity. The polymer molecular weight in step polymerization can be affected by solvent if the polymer is only partially soluble in the solvent and polymer precipitates prematurely.

c) The degree of polymerization is first order in $[\text{M}]$ for most but not all polymerizations.

d) The polymerization rate increases with increasing temperature for all except some cationic polymerizations.

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

7. F_1 is calculated from pairs of monomer ratios (since equimolar!) for $f_1 = f_2 = 0.5$ for each of the

Case	1	2	3	4	5	6	7
F_1	0.478	0.0909	0.216	0.435	0.500	0.375	0.111

8. a) The reaction of boron trifluoride with the more reactive epichlorohydrin forms the corresponding secondary and tertiary oxonium ions. The latter proceed to initiate the polymerization of THF. The formation of initiating species directly from THF (in the absence of epichlorohydrin) is slower.
- b) Water and boron trifluoride constitute the initiating system, but water is also a terminating agent by transfer of HO^\cdot .