Exam (CHEM-E2100 Polymer Synthesis, 5 cr) 24.10.2016

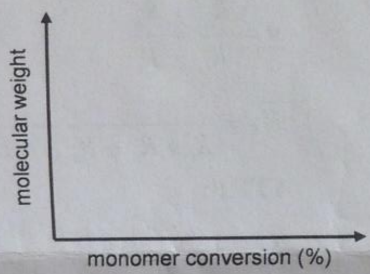
Answer to **all** questions (you can answer also in Finnish).

1. Preliminary assignment:

Summary and key topics of the polymer synthesis course (use max. one A4, both sides). **(6 p)**

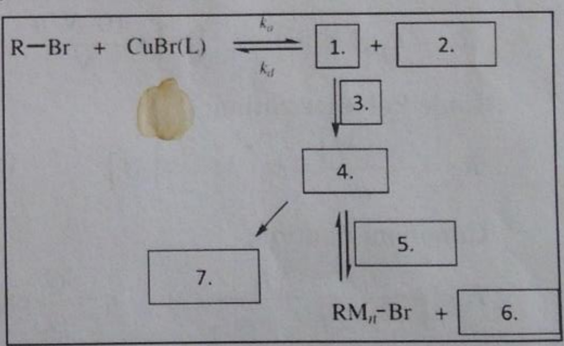
2. Please define briefly:

a) "Grafting to" in bioconjugation? **(1 p)**
b) Kinetic chain length in radical polymerization? **(1 p)**
c) Chain transfer agent? Give an example. **(1 p)**
d) Briefly: divergent and convergent synthesis of dendrimers? **(1 p)**
e) Present the variation of molecular weight with conversion in the case of (i) ideal chain-growth polymerization; (ii) a controlled chain-growth polymerization; (iii) a partially controlled chain-growth polymerization and (iv) a step-growth polymerization. Draw the typical plots to the adjacent graph: **(2 p)**



3. Explain:

a) The principle, benefits and kinetics of emulsion polymerization. **(3 p)**
b) Describe the mechanism of Atom Transfer Radical Polymerization (ATRP) by explaining what reactions/reactants occur in boxes 1.-7. Comment also the advantages of ATRP. **(3 p)**



4. Sebacic acid HOOC-$(CH_2)_8$-COOH and hexamethylene diamine H_2N-$(CH_2)_6$-NH_2 are polymerized in open batch reactor at 230 °C. $M(C_{10}H_{18}O_4) = 202.3$ g/mol, $M(C_6H_{16}N_2) = 116.2$ g/mol.

a) Present the chemical equation for the reaction. **(2 p)**
b) Calculate the number average degree of polymerization X_n and number average molecular weight M_n when extent of the reaction is 0.99 and monomers are in stoichiometric amount. **(2 p)**
c) What is the number average degree of polymerization X_n at $p = 0.99$ if sebacic acid is in excess and the stoichiometric ratio is $r = 0.99$. **(2 p)**

CHEM-E2100 Polymer Synthesis

$n = \frac{m}{M}$ $c = \frac{n}{V}$ $\rho = \frac{m}{V}$ $V_m = \frac{n}{V}$ $pV = nRT$ $k = Ae^{-\frac{E}{RT}}$

$\bar{M}_n = M_0 \times \bar{X}_n$ $p = 1 - \frac{[M]}{[M]_0}$ $R_p = -\frac{d[M]}{dt}$

Step Polymerization:

$\bar{X}_n = \frac{[M]_0}{[M]}$ $\bar{X}_n = \frac{1+r}{1+r-2rp}$ $r = \frac{N_{A,0}}{N_{B,0}}, r<1$ $r = \frac{N_A}{N_B + 2N_{B'}}$ $p_c = \frac{2}{f_{avg}}$ $f_{avg} = \frac{\sum N_i f_i}{\sum N_i}$

Chain Polymerization:

$R_i = -\frac{d[I]}{dt} = k_i[M]\times[R\cdot] = 2f \times k_d[I]$ $R_t = 2k_t[M\cdot]^2$ $[I] = [I]_0 e^{-k_d t}$

$R_p = -\frac{d[M]}{dt} = k_p[M]\times[M\cdot]$ $[M\cdot] = \sqrt{\frac{R_i}{2k_t}}$ $\tau = \frac{[M\cdot]}{R_t}$

$\nu = \frac{R_p}{R_i} = \frac{R_p}{R_t}$ $\bar{X}_n = 2\nu$ (combination) $\bar{X}_n = \nu$ (rearrangement)

$\bar{X}_n = \frac{R_p}{R_t + R_{ts} + R_{tr,M} + R_{tr,S}}$ $\frac{1}{\bar{X}_n} = \frac{R_t}{2R_p} + C_M + C_S\frac{[S]}{[M]} + C_I\frac{[I]}{[M]}$

ATRP:

$R_p = -\frac{d[M]}{dt} = \frac{k_p K[M][I][Cu^+]}{[Cu^{2+}]}$ $\bar{X}_n = \frac{p[M]_0}{[I]_0}$ $\frac{\bar{X}_w}{\bar{X}_n} = 1 + \frac{1}{\bar{X}_n}$

Emulsion Polymerization:

$R_p = k_p[M][P\cdot]$ $[P\cdot] = \frac{10^3 N'\bar{n}}{N_A}$ $r_p = k_p[M]$ $r_i = \frac{R_i}{N}$ $\bar{X}_n = \frac{r_p}{r_i}$

Ionic Polymerization:

$R_p = -\frac{d[M]}{dt} = k_p[M^-]\times[M]$ $\bar{X}_n = \frac{[M]}{[I]}$ $\frac{\bar{X}_w}{\bar{X}_n} = 1 + \frac{1}{\bar{X}_n}$

Copolymerization:

$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$ $r_1 = \frac{Q_1}{Q_2}\exp[-e_1(e_1 - e_2)]$

Finemann&Ross: $\frac{f_1(1-2F_1)}{F_1(1-f_1)} = \frac{f_1^2(F_1-1)}{F_1(1-f_1)^2}\times r_1 + r_2$

Constants:

$R = 8{,}3145$ J/(K mol) $N_A = 6{,}022\times10^{23}$ mol^{-1} $g = 9{,}80665$ m/s^2

0°C = 273,15 K 1 bar = 10^5 Pa

Molecular Weights (g/mol):

H	1,008	C	12,011	N	14,007	O	15,999
Al	26,982	Cl	35,453	Ti	47,867	Zr	91,224