Organic Chemistry – Exercise 9 Mastersheet

Distribution: December 12, 2024
Help: December 19 2024
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1. A sample contains the following polymer chains.

Number of chains	Molar mass (g/mol)
100	10,000
1000	20,000
10	50,000

   a. Calculate the number-average molar mass M_n of the population.
   The number-average molar mass is calculated as:
   $M_n = (\Sigma n_i M_i) / \Sigma n_i$
   - n_i: Number of chains of type i
   - M_i: Molar mass of chains of type i
   M_n = 19369 g/mol

   b. Calculate the weight-average molar mass M_w of the population.
   The weight-average molar mass is calculated as:
   $M_w = (\Sigma n_i M_i^2) / \Sigma n_i M_i$
   M_w = 20233 g/mol

   c. Calculate the dispersity of the population.
   Dispersity (M_w / M_n) = 1.04

2.

   a. What are the critical parameters to ensure that you obtain high molar masses polymers in step-growth polymerization?

   According to the carothers equation, to achieve high molar mass polymers in step-growth polymerization, the following critical parameters must be ensured:
   Stoichiometric Balance: A precise 1:1 ratio of reactive functional groups is essential to maximize polymerization.
   High Conversion Rates: Polymer molar mass grows significantly only when conversion exceeds 99%.

b. The polycondensation between a diacid and a diol leads to the formation of a linear polyester. What is the resulting polymer architecture if glycerol (1,2,3-propanetriol) is used instead of a diol?

If glycerol (1,2,3-propanetriol) is used instead of a diol, the resulting polymer forms a network due to glycerol's three hydroxyl groups, leading to cross-link formation.

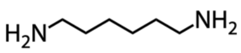
c. Why are high molar masses of polymers desirable with regard to the resulting materials properties?
High molar masses of polymers are desirable because they significantly improve the mechanical and physical properties of materials.
Mechanical Strength: Higher molar mass polymers exhibit increased tensile strength and toughness due to longer chains, which create more entanglements and intermolecular interactions.
Elasticity: Polymers with high molar mass are more elastic, enabling better recovery from deformation, which is essential for rubbers and fibers.
Viscosity and Processing: High molar mass polymers contribute to higher viscosity in melts and solutions, which is critical for processes like fiber spinning, extrusion, and film formation.
Barrier Properties: Longer polymer chains create fewer gaps and pathways for diffusion, leading to better barrier properties in packaging applications.

3. In a polycondensation reaction, 20 g of hexamethylene diamine (1,6-diaminohexane) and 20 g of adipic acid (1,6-hexandioic acid) were added. After 5 min, the remaining amount of unreacted amines was found to be 30 mol% of that of the initial reaction mixture (t = 0 min).

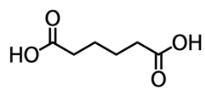
a. What polymer family does the product belong to ?
Polyamide

b. Calculate the number-average degree of polymerization after 5 min.

c. What will be the theoretical number-average degree of polymerization after *very long* reaction times? Note: the limiting functional groups define the maximum possible conversion.



$C_6H_{16}N_2$
M = 116.2 g/mol
20 g (0.172 mol)



$C_6H_{10}O_4$
M = 146.1 g/mol
20 g (0.137 mol)

stoichiometric imablance: $r = 0.8$

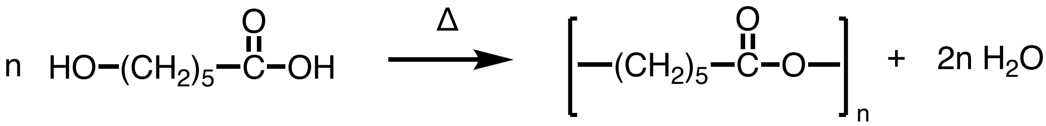
consumed at t = 5 min: $0.172\ mol - 0.3 \cdot 0.172\ mol = 0.120\ mol$

conversion p: $p = \frac{0.120\ mol}{0.137\ mol} = 0.88$

$\overline{X}_n(t = 5\ min) = \frac{1+r}{1+r-2pr} = 4.6$ $\overline{X}_n(t = \infty) = \frac{1+r}{1+r-2pr} = 9$

d. What are the functional group(s) at the chain ends in that case?
Since there is an excess of hexamethylene diamine, the end groups will be amines.

4. Polyester fibres for textiles can, in principle, be produced from ω-hydroxycaproic acid.



a. If the initial 100 mol of the hydroxyacid are reduced to 2 mol after 10 h of reaction time, calculate:

i. The number-average molar mass M_n.
p = 0.98
$$\bar{M}_n = \bar{X}_n M_o = \frac{M_o}{1-p} = \frac{114}{0.02} = 5700$$

ii. The weight-average molar mass M_w.
$$\bar{M}_w = X_w M_o = M_o\left[\frac{1+p}{1-p}\right] = 114\left[\frac{1.98}{0.02}\right] = 11286$$

iii. The probability that the reaction mixture contains tetramers.
$$P_x = p^{x-1}(1-p)$$
$$= (0.98)^{4-1}(1-0.98) = 0.019$$

iv. The weight fraction of these tetramers.
$$w_x = x(p^{x-1})(1-p)^2$$
$$= 4(0.98)^3(0.02)^2 = 1.51 \times 10^{-3}$$

b. As a result of secondary reactions of the hydroxyl groups, a 5% excess of the carboxylic acid is present in the reaction mixture. Calculate the number-average molar mass for the same conversion than in question a.

$$\bar{X}_n = \frac{1+r}{2r(1-p)+1-r}$$
$$r = \frac{100}{105} = 0.95$$
$$\bar{X}_n = \frac{1+0.95}{2(0.95)(1-0.98)+1-0.95} = 22.16$$
$$\bar{M}_n = \bar{X}_n M_o = 2526$$