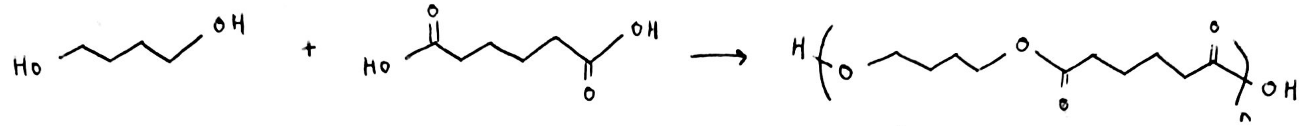
Ch/ChE 147

Problem Set 1

due Jan. 25, 2018

1 (A) 

polyester

(B) diol : A-A, diacid : B-B

$$A\text{-}A + B\text{-}B \longrightarrow \left(aabb \right)_n = \left(C_{10}H_{16}O_4 \right)_n$$

- The molecular weight of the repeat unit (aabb) is 200 g/mol.

- p = fraction of reacted A groups = fraction of reacted B groups

$$\bar{X}_n = \frac{1}{1-p}$$

Note that $\bar{X}_n$ (the number-average number of repeats) counts the number of <u>ab</u> ~~units~~, not aabb units. Therefore, in order to get M_n, we should multiply $\bar{X}_n$ by the average molecular weight of the two kinds of units in ~~the~~ each repeat : $200/2 = 100$ g/mol

- $M_n = 100 \text{ g/mol} \cdot \bar{X}_n = 5000 \Rightarrow \bar{X}_n = 50$

- To get $M_n = 5000$ g/mol, $p = 1 - \frac{1}{\bar{X}_n} = 1 - \frac{1}{50} = 0.98$

(C) From the notes, recall that we defined N_A^o and N_B^o to be the initial numbers of A and B functional groups, respectively. Here, we lose 0.5 mol % of A-A, so $N_A^o = 0.995$ mol, $N_B^o = 1.000$ mol

$$\gamma = N_A^o / N_B^o = 0.995$$

$$\bar{X}_n = \frac{\gamma + 1}{\gamma + 1 - 2\gamma p} = \frac{0.995 + 1}{0.995 + 1 - 2(0.995 \times 0.98)} = 44.5$$

$$M_n = 44.5 \times 100 \text{ g/mol} = 4450 \text{ g/mol}$$

1 (D) We can compensate for the loss in (C) by carrying out the polymerization to a higher extent of reaction.

$$\overline{X}_n = \frac{\gamma + 1}{\gamma + 1 - 2\gamma p} = 50$$

$$\Rightarrow p = \frac{(\gamma+1)(\overline{X}_n - 1)}{2\overline{X}_n \gamma} = \frac{(0.995+1)(50-1)}{2(50)(0.995)} = 0.9825$$

(E) Acetic acid is a monofunctional reagent (i.e., a "chain stopper"), denoted B'.

$N_{B'}$ = number of monofunctional acid groups = (2 mol)(0.01) = 0.02

N_B = number of acid groups in B-B monomers = 1.98

N_A = 2.00 (since there is no other stoichiometric imbalance)

$$\gamma' = \frac{N_A^{\circ}}{N_B^{\circ} + 2N_{B'}^{\circ}} = \frac{2.00}{1.98 + 2(0.02)} = 0.99$$

Use the equation for p in part (D), replacing γ with γ':

$$p = \frac{(\gamma'+1)(\overline{X}_n - 1)}{2\overline{X}_n \gamma'} = \frac{(0.99+1)(50-1)}{2(50)(0.99)} = 0.985$$

2. $A + B \longrightarrow AB + C$

99% yield $\Rightarrow p = 0.99$

(A) $A\text{-}A + B\text{-}B \longrightarrow X_1 \left(\underbrace{A\text{-}A}_{\text{1 structural unit}} \overset{\text{new bond}}{-} \underbrace{B\text{-}B}_{\text{1 structural unit}} \right) X_2$ $\qquad X_1 + X_2 = C$

18 g/mol

$$\overline{X}_n = \frac{\#\text{ structural units}}{1\text{ chain}} = \frac{1}{1-p} = \frac{1}{1-0.99} = 100$$

average molecular weight of a repeat unit =

$$M_0 = \frac{(\text{m.w. } A\text{-}A) + (\text{m.w. } B\text{-}B)}{2} - (\text{m.w. } C) = \left(\frac{72+98}{2}\right) - 18 = 67 \text{ g/mol}$$

$$M_n = M_0 \overline{X}_n = (67 \text{ g/mol})(100) = 6700 \text{ g/mol}$$

$$Đ = 1 + p = 1 + 0.99 = 1.99$$

$$M_w = Đ M_n = 13300 \text{ g/mol}$$ (rounded to three sig. figs)

another way to obtain M_0:

$A\text{-}A + B\text{-}B \longrightarrow A\boxed{\text{-}A \overset{\text{new bond}}{-} B\text{-}}B + C$

72 g/mol, 98 g/mol, 152 g/mol, 18 g/mol

after 1 step: + 80 g/mol

$A\text{-}A\text{-}B\text{-}B + A\text{-}A \longrightarrow A\text{-}A\text{-}B\boxed{\text{-}B \underset{\text{new bond}}{-} A\text{-}}A + C$

152 g/mol, 72 g/mol, 206 g/mol

after 2 steps: + 134 g/mol

$\Rightarrow$ avg. increase in M_n per step = +67 g/mol

$M_n = (67 \text{ g/mol})(100 \text{ units}) = 6700 \text{ g/mol}$

(B) $2\ A\text{-}B \longrightarrow X_1 - A\left(\underbrace{B\text{-}A}_{\text{1 structural unit}}\right)_n B - X_2$

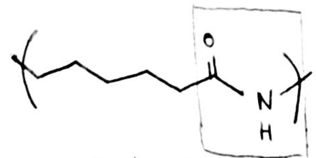
$$\overline{X}_n = \frac{1}{1-p} = 100$$

$$M_0 = (\text{m.w. } A\text{-}B) - (\text{m.w. } C) = 85 - 18 = 67 \text{ g/mol}$$

$$M_n = M_0 \overline{X}_n = (67 \text{ g/mol})(100) = 6700 \text{ g/mol}$$

$Đ = 1 + p = 1.99$, $M_w = Đ M_n = 13300 \text{ g/mol}$

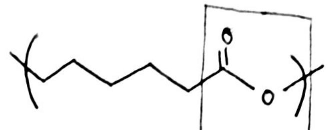
3.



nylon 6 amide

versus

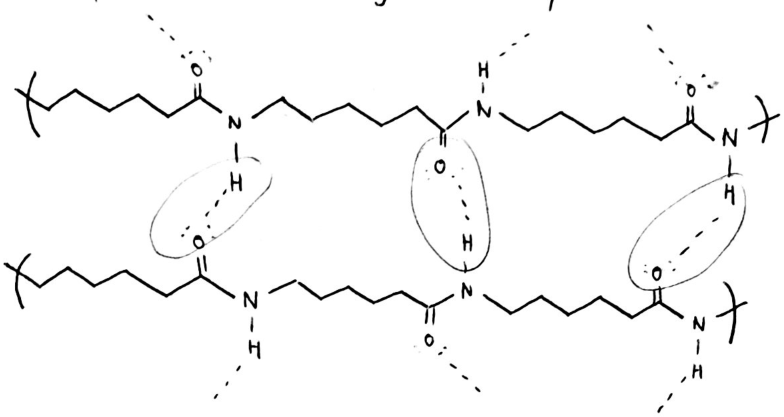
ester



poly (ε-caprolactone)

Only difference in the repeat unit: amide (nylon 6) vs. ester (poly (ε-caprolactone))

T_m is higher for nylon 6 than for poly (ε-caprolactone), indicating that the nylon 6 crystallites are more stable to increasing temperature. This can be explained by the ability of amide linkages in nylon 6 to form hydrogen bonds:



Poly (ε-caprolactone), the polyester analogue, cannot form H-bonds.

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4 (A) The second column shows the weight fraction (w_i) of chains of length i ~~w_i~~.

Let N_i = number of chains of length i.

M_i = molecular weight of chains of length i (i.e., the third column)

In part (A), we want to know which fraction has the largest N_i.

$$w_i = \frac{N_i M_i}{\sum_i N_i M_i} = \frac{i N_i}{\sum_i i N_i}$$

$\Rightarrow N_i \propto \frac{w_i}{M_i}$ since $\sum_i N_i M_i$ is the total weight of all chains, a constant

Refer to the spreadsheet. Fractions 1 and 2 have the largest values of ~~N_i~~ w_i/M_i, and therefore the largest number of chains.

Fraction Number	Weight Fraction	Molecular Weight (g/mol)	w_i / M_i	$w_i M_i$
1	0.08	28,000	2.86E-06	2240
2	0.14	49,000	2.86E-06	6860
3	0.19	80,000	2.38E-06	15200
4	0.13	95,000	1.37E-06	12350
5	0.08	135,000	5.93E-07	10800
6	0.10	165,000	6.06E-07	16500
7	0.07	200,000	3.50E-07	14000
8	0.12	240,000	5.00E-07	28800
9	0.06	385,000	1.56E-07	23100
10	0.03	460,000	6.52E-08	13800
			1.17E-05	143650
			$\Sigma (w_i / M_i)$	$\Sigma (w_i M_i)$

$\Sigma w_i = 1$

4 (B) $$M_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{\sum w_i}{\sum (w_i/M_i)} = \frac{1}{\sum (w_i/M_i)}$$

From the spreadsheet: $M_n = (1.17 \times 10^{-5} \text{ mol/g})^{-1} = 8.53 \times 10^4 \text{ g/mol}$

(C) $$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum w_i M_i}{\sum w_i} = \sum w_i M_i$$

From the spreadsheet: $M_w = 1.44 \times 10^5 \text{ g/mol}$

(D) dispersity: $Đ = M_w/M_n = 1.68$

5.

	osmometry	light scattering
(A) M_n	✓	
(B) M_w		✓
(D) A_2	✓	✓

(A) The absolute M_n can be determined from osmometry data:

$$\frac{\pi}{cRT} = \frac{1}{M_n} + A_2 c$$

Note: Make sure to use the value of R consistent with the units.

For example, if π is in units of dyn/cm^2 and c in units of g/cm^3,

$$R = 8.314 \times 10^7 \ erg\ K^{-1} mol^{-1} = 8.314 \times 10^7 \ dyn \cdot cm \cdot K^{-1} mol^{-1}$$

Calculate $\frac{\pi}{cRT}$ and plot versus c. See the attached spreadsheet.

$$M_n = \frac{1}{\text{y-intercept}} = \frac{1}{2.40 \times 10^{-7}} = 4.17 \times 10^{6}/mol$$

$$A_2 = \text{slope} = 2.33 \times 10^{-5}$$

(B) The absolute M_w can be determined from light-scattering data.

$$\frac{Kc}{R_\theta} = \frac{1}{M_w} + 2 A_2 c$$

assume $n \approx n_0$ in dilute solution

$$K = \text{optical constant} = \frac{4\pi n^2}{\lambda^4 N_{Av}} \left(\frac{dn}{dc}\right)^2 = \frac{4\pi (1.4)^2 (0.10\ cm^3/g)^2}{(\underset{cm}{5.5 \times 10^{-5}})^4 (\underset{1/mol}{6.022 \times 10^{23}})}$$

$$= 1.404 \times 10^{-7} \ \frac{cm^2\ mol}{g^2}$$

5 (B) Calculate $\frac{Kc}{R_0}$ and plot versus c. See the attached spreadsheet.

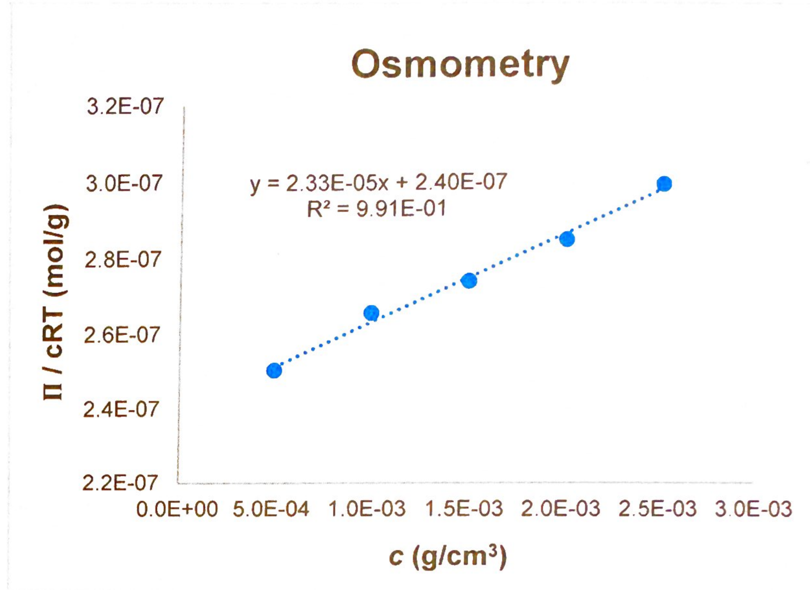
$$M_w = \frac{1}{\text{y-intercept}} = \frac{1}{1.21 \times 10^{-7}} = 8.26 \times 10^{6} \ g/mol$$

$$A_2 = \frac{\text{slope}}{2} = 2.31 \times 10^{-5}$$

(C) $Đ = M_w / M_n = 1.98$

(D) $A_2 = 2.3 \times 10^{-5}$

c (g/cm^3)	Π (dyn/cm^2)	Π / cRT (mol/g)
5.00E-04	3.08	2.50E-07
1.00E-03	6.53	2.65E-07
1.50E-03	10.1	2.74E-07
2.00E-03	14.0	2.84E-07
2.50E-03	18.4	2.99E-07



c (g/cm^3)	R_θ (1/cm)	Kc / R_θ (1/cm)
5.00E-04	4.90E-04	1.43E-07
1.00E-03	8.40E-04	1.67E-07
1.50E-03	1.10E-03	1.91E-07
2.00E-03	1.30E-03	2.16E-07
2.50E-03	1.50E-03	2.34E-07