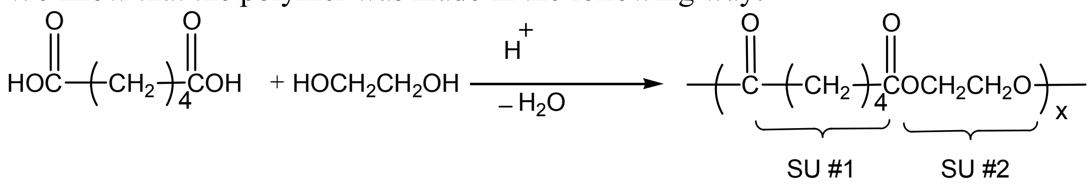
3.034 Practice Set A   Solutions

We know that the polymer was made in the following way:

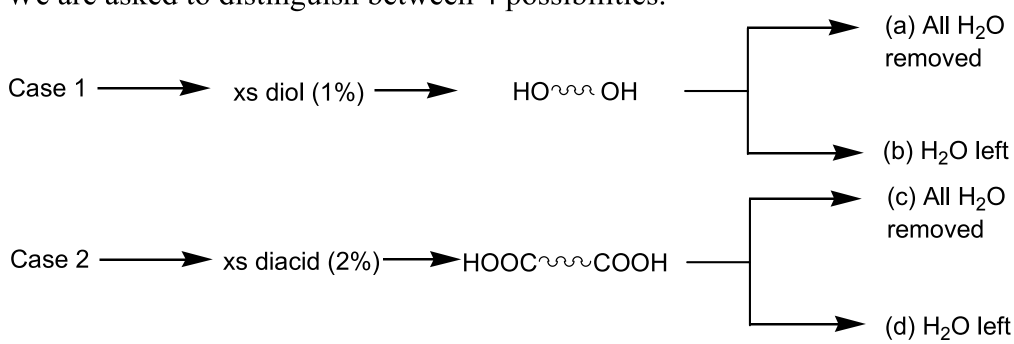


$\overline{M_n} \approx 8300$ g/mol

We know that $\overline{M_n} = \overline{D}_{pn} \cdot M_o$, $M_o = (M_{SU\#1} + M_{SU\#2})/2 = 86$ g/mol

Note M_o is <u>not</u> the repeat unit molecular weight and M_o is based on the molecular weight of the structural units <u>not</u> the original monomers.

We are asked to distinguish between 4 possibilities.



Let us first consider Case 1.

(a) 1% xs diol, all H_2O removed

$\overline{D}_{pn} = (1+r)/(1+r-2pr)$ where $r = [COOH]_o/[OH]_o$, remember r is always less than one, and p is the extent of rxn of COOH groups and varies from $0 \rightarrow 1$.

If no H_2O, $p \rightarrow 1$ and $\overline{D}_{pn}$ max = $(1+r)/(1-r)$

Calculate r (on a 100 mol basis)
$r = 100/101 \rightarrow r \approx 0.99$ (watch significant figures!)

Calculate $\overline{D}_{pn} = (1+r)/(1-r) = (1+0.99)/(1-0.99) = 199$

$$\overline{M_n} = 86 \times \overline{D}_{pn} = 17{,}114 \text{ g/mol}$$

(b) 1% xs diol, $[H_2O]/[OH]=0.05$

Again $\overline{D}_{pn} = (1+r)/(1+r-2pr)$ where $r = [COOH]_o/[OH]_o$
But here $p \neq 1$ $\rightarrow$ need to use equilibrium considerations to find p.

$k_{eq} = 1.0 = \frac{[H_2O][-COO-]}{[OH][COOH]}$ again p is the extent of rxn of COOH groups not <u>OH</u> groups

$[-COO-] = p[COOH]_o$
$[COOH] = (1-p)[COOH]_o$
$[OH] = (1-p_B)\,[OH]_o = (1-pr)*[COOH]_o/r$ $p_B \rightarrow$ the extent of rxn of OH groups, $p \neq p_B$,
$p_B = pr$

Now we can go back to the k_{eq} expression.

$$k_{eq} = 1.0 = \frac{[H_2O][-COO-]}{[OH][COOH]} = \frac{P[COOH]_o x}{(1-P)[COOH]_o} \qquad \text{where } x = \frac{[H_2O]}{[OH]}$$

Solve for p: $p = 1/(1+x)$
When $x = 0.05$, $p = 0.95$

Calculate $\overline{D}_{pn} = (1+r)/(1+r-2pr) = 19$ with $p=0.95$ and $r=0.99$

$\overline{M}_n = 86 \times 19 = 1{,}640$ g/mol

Now let us consider Case 2

(c) 2% xs diacid, all H_2O removed

$\overline{D}_{pn} = (1+r)/(1+r-2pr)$ again, $p \rightarrow 1$ and $\overline{D}_{pn} = (1+r)/(1-r)$
However, here $r = [OH]_o/[COOH]_o$, because the acid is in xs and $r \leq 1.0$!
We also need to redefine p,
p = the extent of rxn of OH groups and p varies from $0 \rightarrow 1$

here $r = 100/102 \rightarrow r = 0.98$

Calculate $\overline{D}_{pn} = (1+r)/(1-r) = (1+0.98)/(1-0.98) = 99$

$\overline{M}_n = 86 \times 99 = 8{,}500$ g/mol

(d) 2% xs diacid, $[H_2O]/[OH]=0.05$

Again $\overline{D}_{pn} = (1+r)/(1+r-2pr)$ where $r = [OH]_o/[COOH]_o$
$p \neq 1 \rightarrow$ need to use equilibrium considerations to find p.

$$k_{eq} = 1.0 = \frac{[H_2O][-COO-]}{[OH][COOH]}$$ remember: p is the extent of rxn of OH groups

$[-COO-] = p[OH]_o$
$[OH] = (1-p)[OH]_o$
$[COOH] = (1-p_B)\,[COOH]_o = (1-pr)*[OH]_o/r$ $p_B \rightarrow$ the extent of rxn of COOH groups

Substitute into the k_{eq} expression.

$$k_{eq} = 1.0 = \frac{p[OH]_o x}{(1-pr)[OH]_o / r} \qquad \text{where } x = \frac{[H_2O]}{[OH]}$$

Solve for p: $p = (1/r)/(1+x) \rightarrow p = 0.97$

Solve for $\overline{D}_{pn} = (1+r)/(1+r-2pr) \approx 26$

$\overline{M}_n = 86 \times 26 = 2{,}260$ g/mol

The closest M_n is 2% diacid, all water removed.

Summary

	r=0.99, P=1	r=0.98, P=1	r=0.99, P=0.95	r=0.98, P=0.97
D_{pn}	199	99	19	26
M_n (g/mol)	17,144	8,500	1,640	2,260