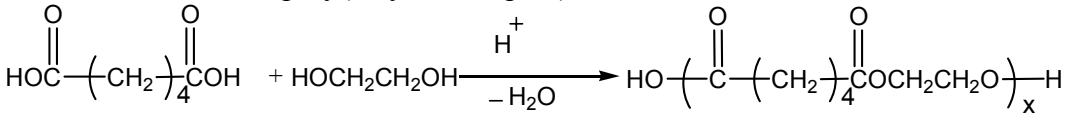
3.034 – solution to quiz #2 (problems 1 and 2 and 3a)

The reaction to make poly(ethylene adipate) is as follows:



$M_n = D_{pn}M_o$ where M_o = 86 g/mol (average molecular weight of 2 structural units in chain).

In this case, an excess of diol (ethylene glycol) was used and all water byproduct was not removed from the reaction. Since all water byproduct was not removed, the maximum extent of reaction (p) possible will be determined by equilibrium.

For a non-stoichiometric reaction (excess diol in this case),

a) $D_{pn}= (1+r)/(1+r-2pr)$ with $r = [COOH]_0/[OH]_0 = 0.99$ (1 % excess)

Note, the extent of reaction (p) is always defined in terms of the limiting functional group, in this case, the COOH group.

p = fraction of COOH groups reacted
1-p = fraction of COOH groups remaining
p_B = fraction of OH groups reacted
$1-p_B$ = fraction of OH groups remaining

$[COOH] = [COOH]_0(1-p)$
[ester linkages] = $p[COOH]_0$
$[OH] =[OH]_0(1-p_B) = ([COOH]_0/r)\cdot(1-pr)$

from the equilibrium equation: $1.0 = ([\text{ester linkages}][\text{water}])/([COOH] [OH])$

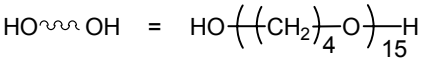
let $[water]/[COOH] = x$
setting $[OH] = ([COOH]_0/r)(1-pr)$ and [ester linkages] = $p[COOH]_0$ and solving for p

gives … $p= 1/(r(1+x))$
with x=0.05 (given) and r=0.99 we get p=0.962

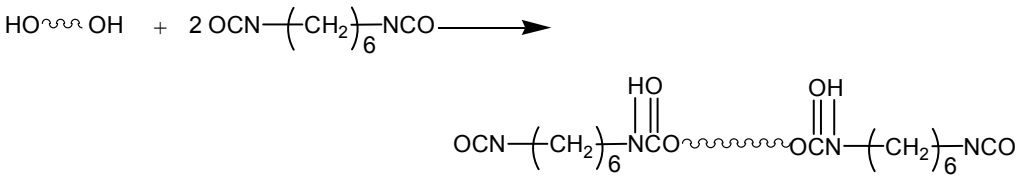
thus, using the above equation for a non-stoichiometric reaction, we get the following

$D_{pn}= (1+r)/(1+r-2pr) = 22$ and $M_n = D_{pn}M_o= 1892$ g/mol

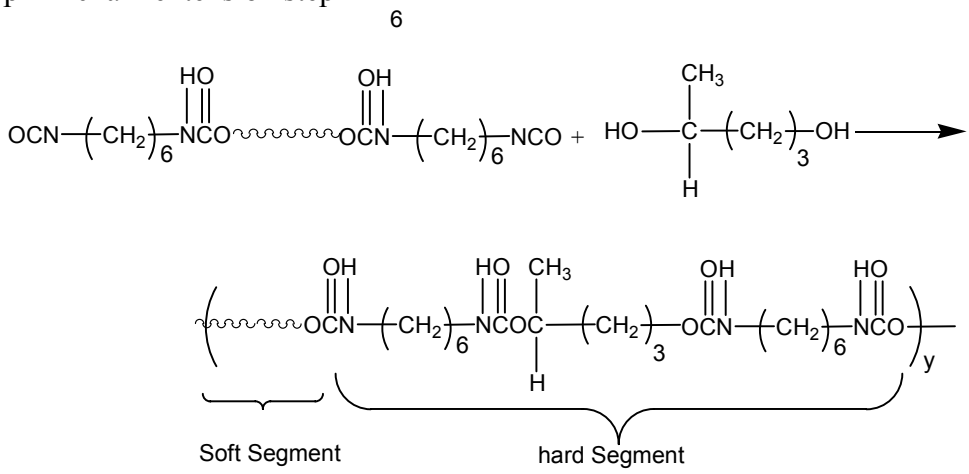
2) Let



Step 1 - endcapping step

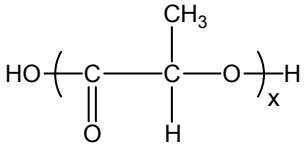


Step 2 – chain extension step



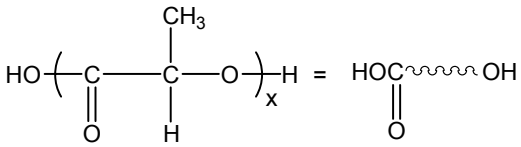
Note: due to the asymmetry of the diol used in the chain extension step, the polymer will be comprised of a random arrangement of head-to-head and head-to-tail linkages in the hard segments.

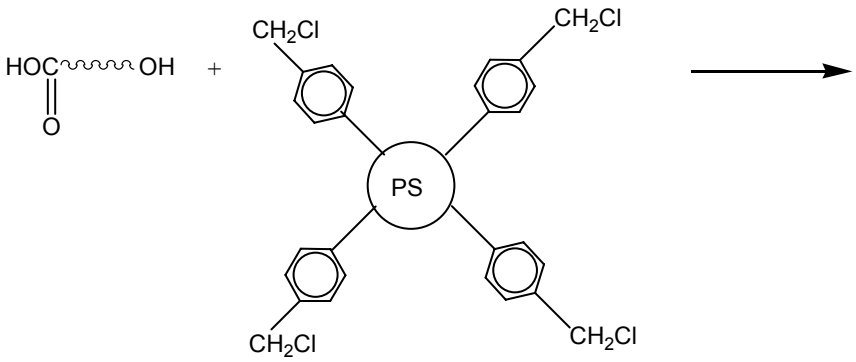
3) poly(lactic acid) is



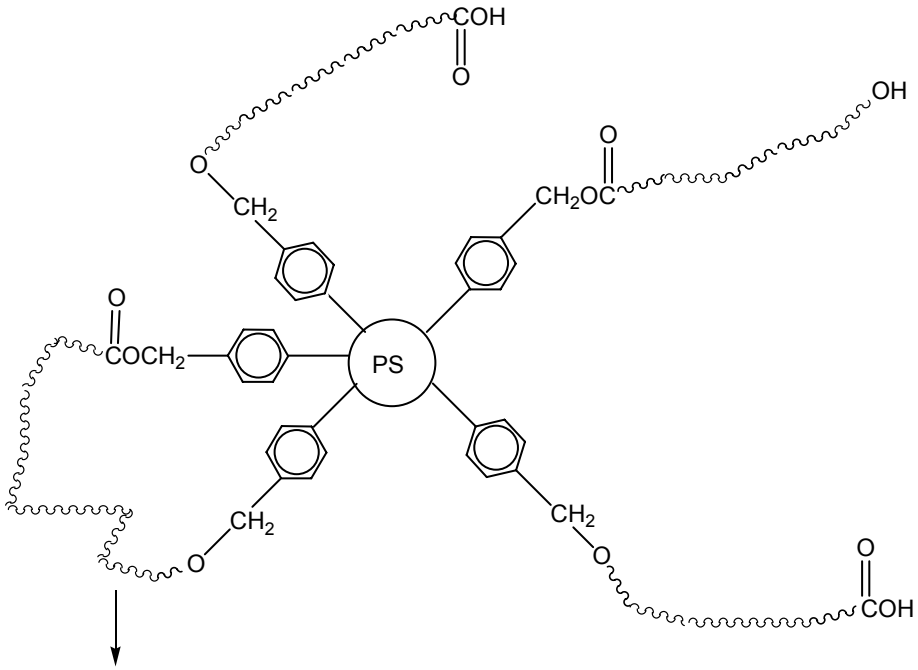
note: in a typical direct esterification reaction, each polymer chain with have on average a –OH and -COOH group for chain ends. Both of these functional groups will react with the active benzyl chloromethyl functional group found on the polystryene beads typically used in a solid phase peptide synthesis.

Let





not to scale



some closed loops may be formed depending on the molecular weight of the poly(lactic acid)