Solutions to Problem Set 1

Chapter 1 recommended practice problems w/ solutions

Poly(methyl acrylate) (?)

5. Star polymers are branched molecules with a controlled number of linear arms anchored to one central molecular unit acting as a branch point. Schaefgen and Flory[§] prepared poly (ε-caprolactam) four- and eight-arm stars using cyclohexanone tetrapropionic acid and dicyclohexanone octapropionic acid as branch points. The authors present the following stoichiometric definitions/relations to relate the molecular weight of the polymer to the concentration of unreacted acid groups in the product. Provide the information required for each of the following steps:

(a) The product has the formula $R\text{-}\{-CO[-NH(CH_2)_5CO-]_y-OH\}_b$. What is the significance of R, y, and b?

(b) If Q is the number of equivalents of multifunctional reactant which react per mole of monomer and L represents the number of equivalents of unreacted (end) groups per mole of monomer, then $\langle y\rangle = (1-L)/(Q+L)$. Justify this relationship, assuming all functional groups are equal in reactivity.

(c) If M_0 is the molecular weight of the repeat unit and M_b is the molecular weight of the original branch molecule divided by b, then the number-average molecular weight of the star polymer is

$$M_n = b\left\{M_0\frac{1-L}{Q+L} + M_b\right\}$$

Justify this result and evaluate M_0 and M_b for the $b=4$ and $b=8$ stars.

(d) Evaluate M_n for the following molecules:

b	Q	L
4	0.2169	0.0018
8	0.134	0.00093

1.5 (a) R = cyclohexanone for b = 4 and bicyclohexanone for b = 8.

b = number of arms in star

y = degree of polymerization of each linear chain

(b) 1 – L = number of equivalents of reacted groups per mole monomer

Q + L = total number of equivalents of "ends" per mole monomer

$$\therefore \text{ ratio } = \frac{\text{number of reacted groups}}{\text{number of ends}} = y$$

(c) For a molecule with b arms

$$\overline{M}_n = bM_{n,arm} + M_{central}$$

and $M_{n,arm} = yM_o = \dfrac{1-L}{Q+L}M_o$

$$M_b = \frac{M_{central}}{b}$$

$$\therefore \overline{M}_n = b\left[M_o\frac{1-L}{Q+L} + M_b\right]$$

6.) Batzer reported the following data for a fractionated polyester made from sebacic acid and 1,6-hexanediol;[1] evaluate M_n, M_w, and M_z.

Fraction	1	2	3	4	5	6	7	8	9
Mass (g)	1.15	0.73	0.415	0.35	0.51	0.34	1.78	0.10	0.94
$M \times 10^{-4}$	1.25	2.05	2.40	3.20	3.90	4.50	6.35	4.10	9.40

1.6 By dividing m_i by M_i, we obtain the number of moles for each fraction, n_i. We then utilize the equations

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i},\quad M_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} \text{ and } M_z = \frac{\sum_i n_i M_i^3}{\sum_i n_i M_i^2}$$

to obtain M_n=29.1 kDa, M_w=46.1 kDa and M_z=62.5 kDa.

8.) Consider a set consisting of 4–8 family members, friends, neighbors, etc. Try to select a variety of ages, genders, and other attributes. Take the mass of each individual (a rough estimate is probably wiser than asking directly) and calculate the number- and weight-average masses for this set. Does the resulting PDI indicate a rather "narrow" distribution? If you picture this group in your mind, do you imagine them all to be roughly the same size, as the PDI probably suggests?

1.8 Example solution (inspired by the characters of Marvel Comics):

Character	Mass (kg)	w_i	$w_i M_i$
Jean Gray	52	0.11	5.7
Rogue	54	0.11	6.2
Bruce Banner	58	0.12	7.1
Elektra	59	0.12	7.3
Spider-Man	75	0.16	11.8
Magneto	86	0.18	15.7
Wolverine	88	0.19	16.5

For the listed characters,

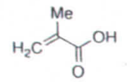
$$M_n = \sum M_i / 7 = 67.5 \text{ kg}$$

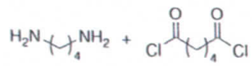
$$M_w = \sum w_i M_i = 70.6 \text{ kg}$$

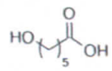
$$PDI = M_w / M_n = 1.04$$

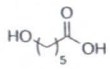
Based on PDI, the selected distribution is quite narrow.

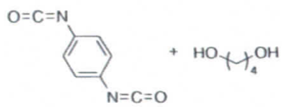
12. Give the overall chemical reactions involved in the polymerization of these monomers, the resulting repeat unit structure, and an acceptable name for the polymer.

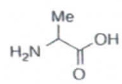
(a) 

(b) 

(c) 

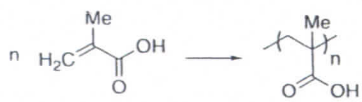
(d) 

(e) 

(f) 

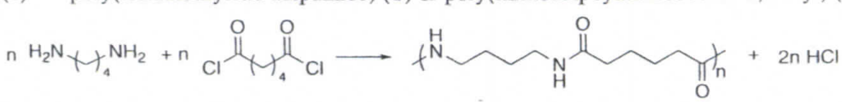
(see corrected solutions at end of problem set)

1.12 (a) poly(methacrylic acid) (T) or poly[1-(carboxy)-1-methylethylene] (I)



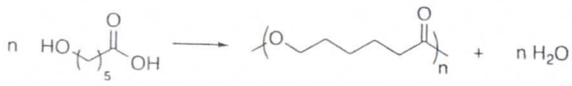
A chain growth process (free radical) through the carbon-carbon double bond; initiation and termination steps are not specified).

(b) poly(tetramethylene adipamide) (T) or poly(iminoadipoyliminobutane-1,4-diyl) (I)



A step growth (polycondensation) process bewteen a diamine and a diacid chloride.

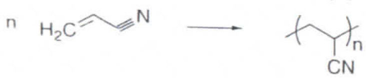
(c) poly(6-hydroxyhexanoic acid) (T) or poly(oxycarbonyl pentamethylene) (I)



A step growth (self-condensation) of an α-hydroxy, ω-carboxy alkane.

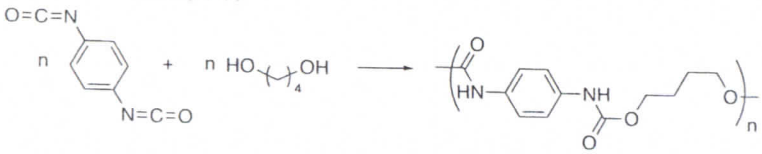
(d) same as (c) by mistake!

It was supposed to be poly(acrylonitrile) (T) or poly(1-cyanoethylene) (I)



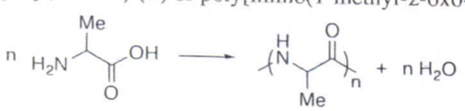
A chain growth process (free radical) through the carbon-carbon double bond; initiation and termination steps are not specified).

(e) poly(tetramethylene phenylurethane) (T) or poly(oxytetramethyleneoxycarbonylimino-1,4-phenyleneiminocarbonyl) (I)



A step growth polymerization (strictly, not a condensation) between a diisocyanate and a diol. Note that in reality the NH groups can react with the NCO groups to produce some crosslinking.

(f) poly(alanine) (T) or poly[imino(1-methyl-2-oxo-ethylene)] (I)



A step growth (self-condensation) of an amino acid.

15. What would be M_w and M_n for a sample obtained by mixing 10 g of polystyrene ($M_w = 100{,}000$, $M_n = 70{,}000$) with 20 g of another polystyrene ($M_w = 60{,}000$, $M_n = 20{,}000$)?

1.15 The mole fractions can be obtained from the sample masses and M_n values:

$$x_1 = \frac{10/70{,}000}{10/70{,}000 + 20/20{,}000} = \frac{1}{8}; \quad x_2 = \frac{7}{8}$$

Therefore for the mixture

$$M_n = \frac{70{,}000}{8} + \frac{7 \times 20{,}000}{8} = 26{,}250$$

The weight fractions are easily seen to be 1/3 and 2/3, giving

$$M_w = \frac{1}{3} \times 100{,}000 + \frac{2}{3} \times 60{,}000 = 73{,}333$$

16. What would M_w and M_n be for an equimolar mixture of tetradecane and decane? (Ignore isotope effects.)

1.16 Tetradecane ($C_{14}H_{30}$) and decane ($C_{10}H_{22}$) have molecular weights of 198 and 142, respectively. For an equimolar mixture, $x_i = 0.5$, and therefore

$$M_n = \frac{1}{2}(198 + 142) = 170$$

The weight fractions are given by the proportion of mass, and therefore

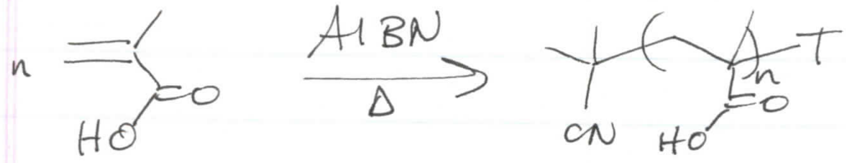
$$M_w = \frac{198}{198+142} \times 198 + \frac{142}{198+142} \times 142 = 174.6$$

The polydispersity is 1.027.

Chem 466

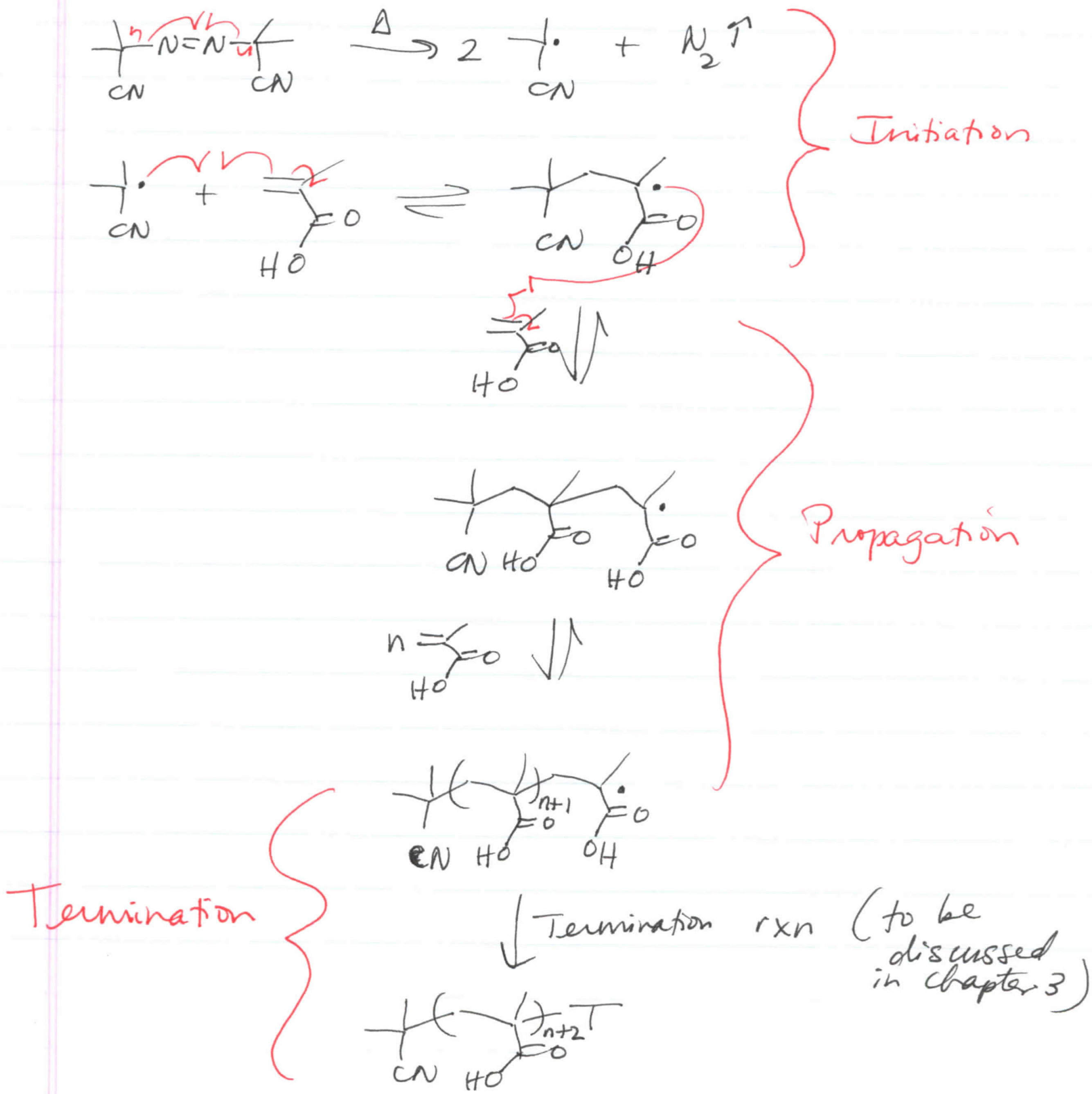
Chapter 1 problem 12

(a)

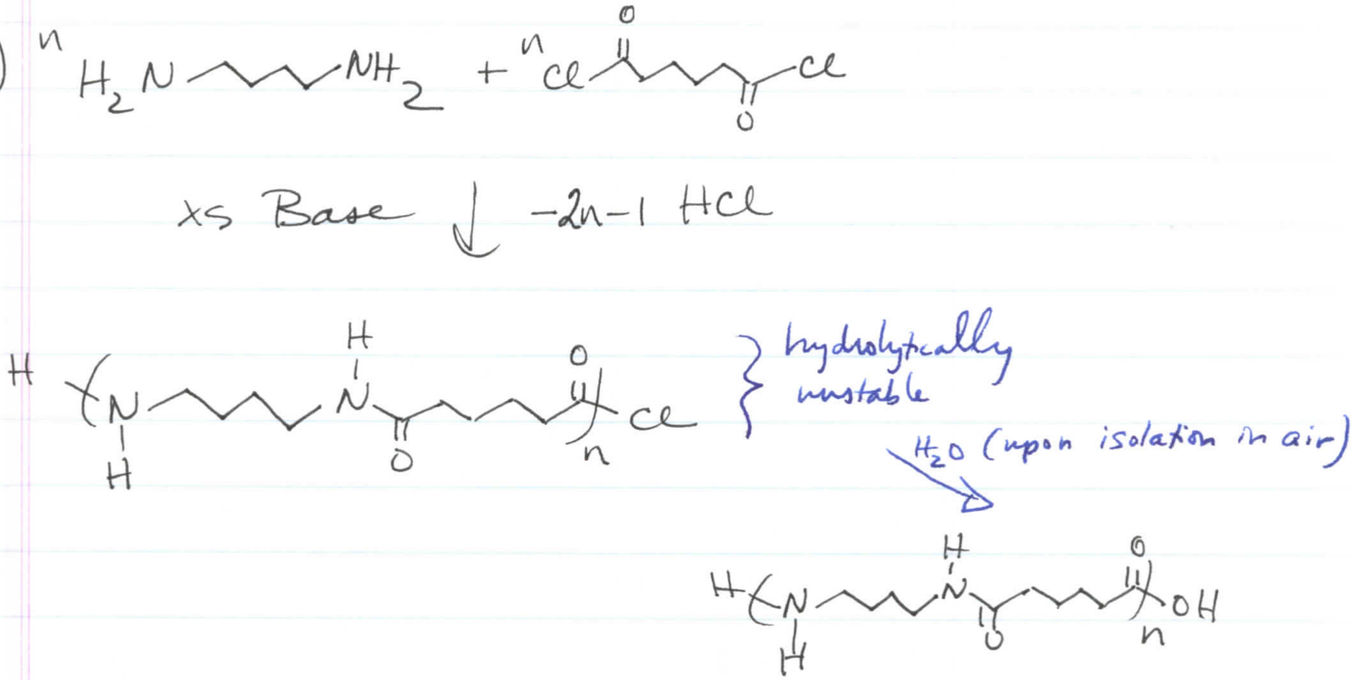


poly(methacrylic acid)

mechanism:

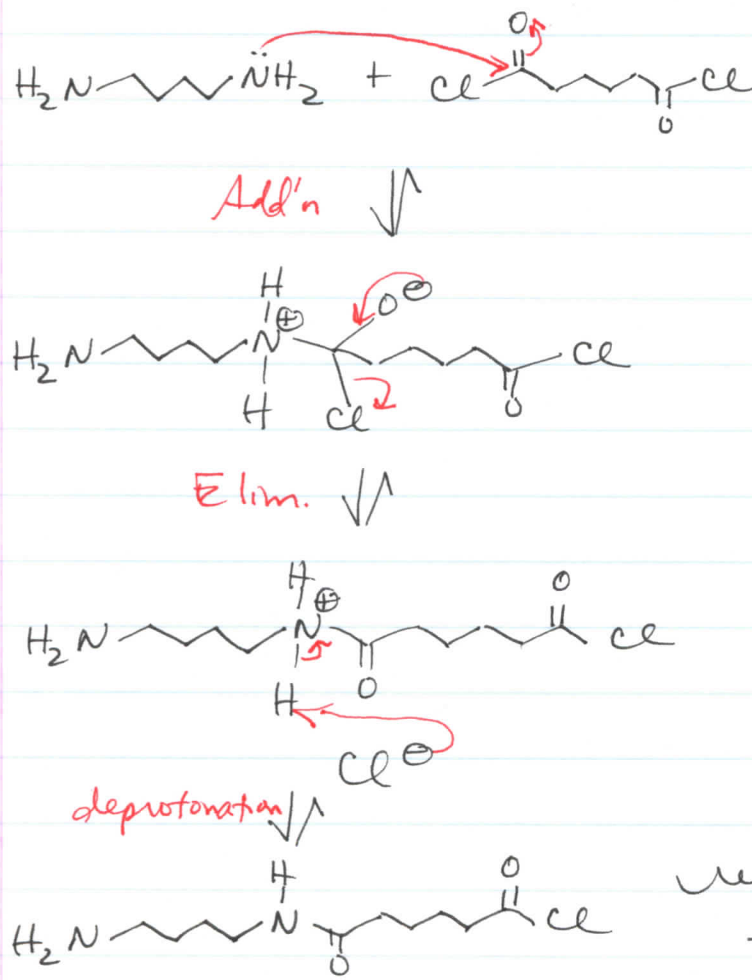


(6)

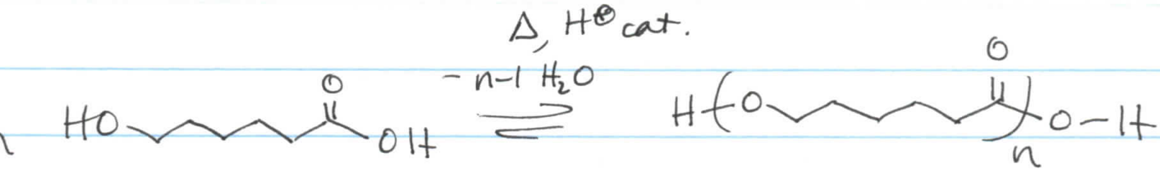


Nylon 4,6
or poly(tetramethylene adipamide)

mechanism:



repeats many times to produce the polymer

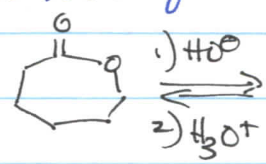
(c) 

poly (6-hydroxyhexanoic acid)

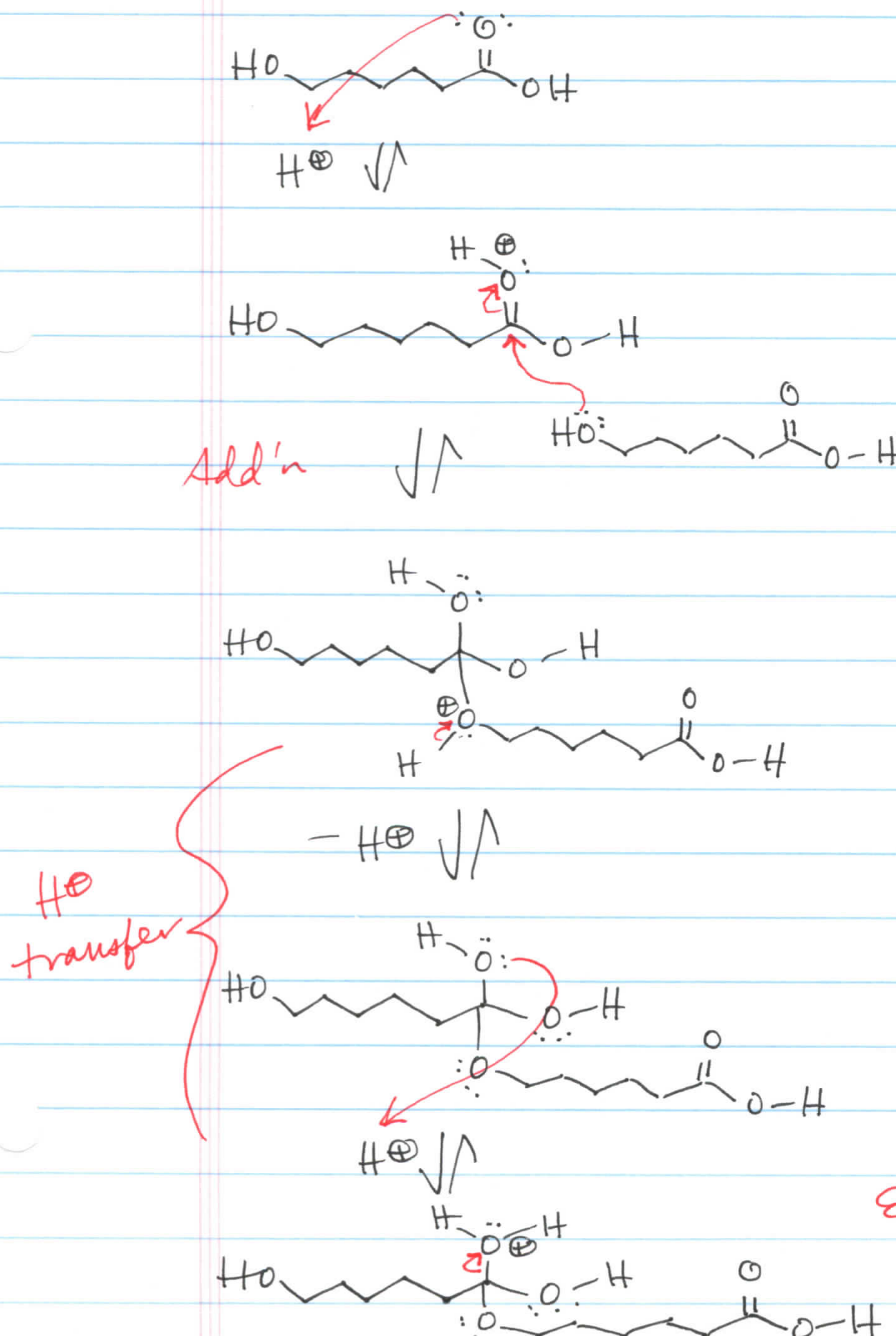
or poly (6-hydroxycaproic acid)

or poly (ε-caprolactone)

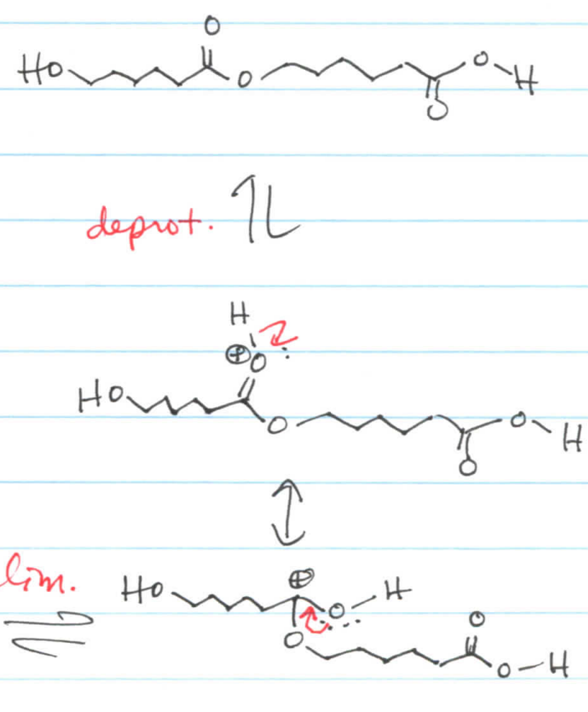
this name is not exactly correct, based upon the monomer used, but the polymer is of the same composition as that from



<u>Mechanism:</u>



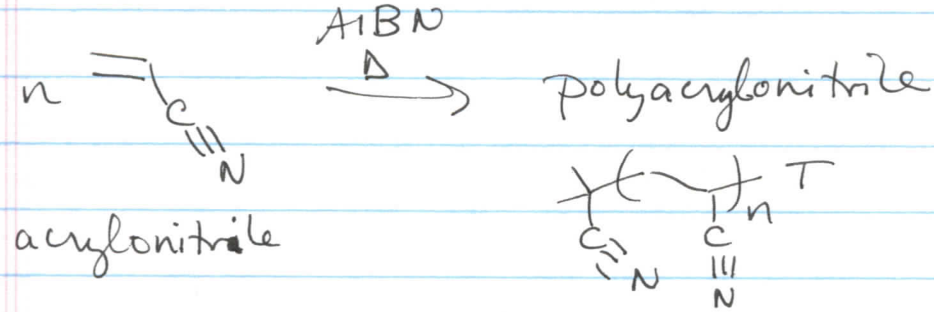
repeats many times to produce polymer



(corrected in 2012 textbook, pH 2nd edition)

2011

(d) mistake in 2011 textbook; was supposed to be



the radical polym. mechanism is the same as for (a)