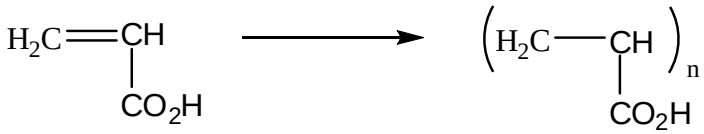
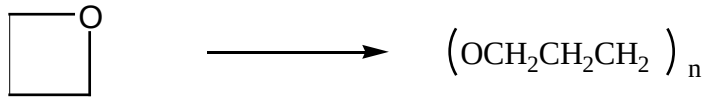
Problem Set 1 Answer Key

1.

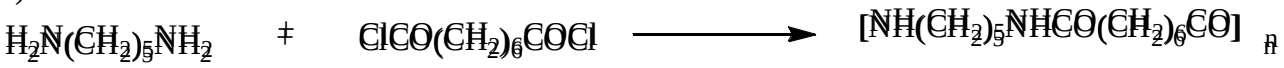
a)



b)



c)



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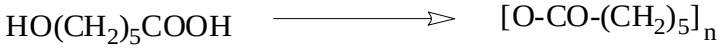
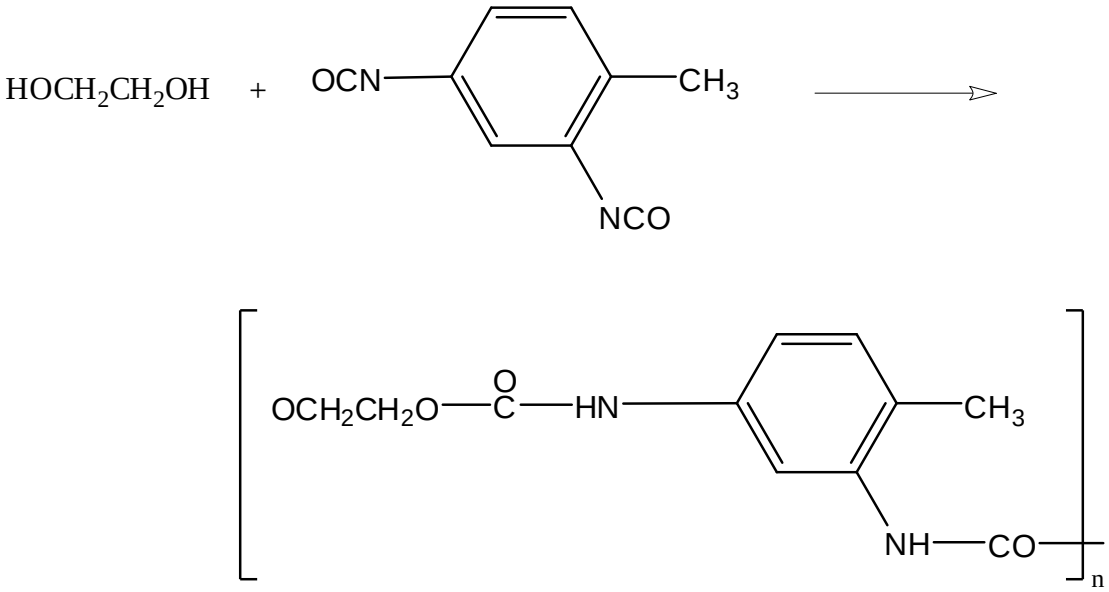
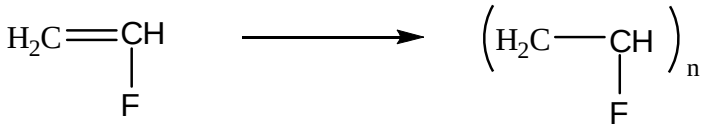


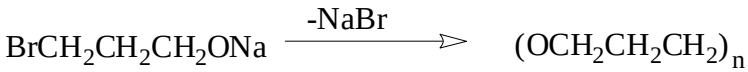
e)

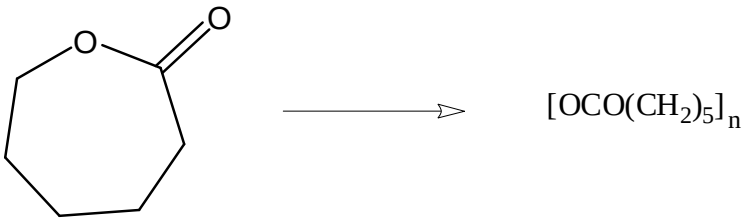


f)



2. The repeating units are shown on the right sides of the equations. Other monomers cannot be used to synthesize the structures in 1a,c,e,f. The polymers in b and d could be synthesized via



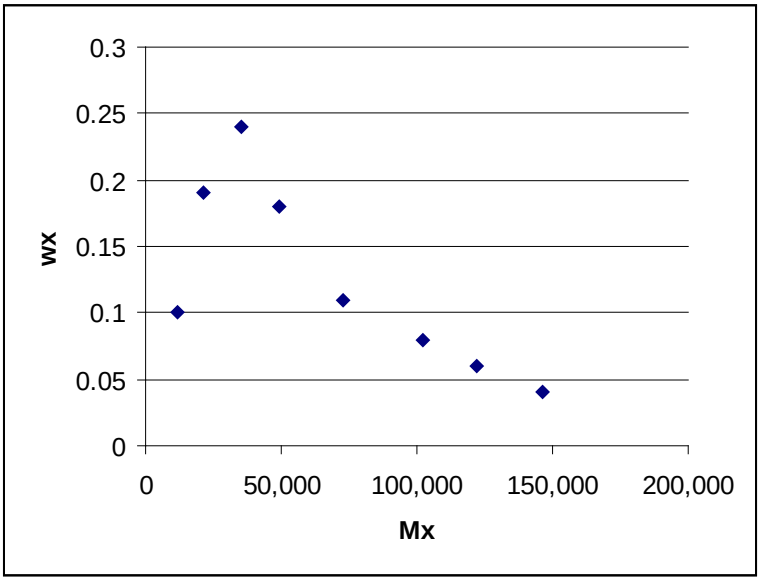


3. Follow the polymerization as a function of conversion by using size exclusion chromatography. Chain polymerization of a C-C double bond monomer produces high molecular weight polymer even at low conversion. The reaction mixture contains only polymer and monomer with no intermediate sized species and the polymer:monomer ratio increased with conversion. Step polymerization shows a continuous increase in product molecular weight with conversion. Various sized species are present at all conversions and high molecular weight polymer is not achieved until conversions above 97-98%. Ring opening polymerization is a chain polymerization which follows a different pathway compared to the chain polymerization of a C-C double bond monomer. Polymer molecular weight increases with conversion and high molecular weights require high conversions, but not as high as step polymerizations.

4. Considering a 100g sample of polymer, one calculates:

M_x	w_x	w_xM_x	weight (g)	$N_x = g/M_x$	$\underline{N}_x = N_x/\Sigma N_x$	$\underline{N}_xM_x$
12,000	0.1	1,200	10	8.30E-04	0.27	3,240
21,000	0.19	3,990	19	9.00E-04	0.29	6,090
35,000	0.24	8,400	24	6.90E-04	0.22	7,700
49,000	0.18	8,820	18	3.70E-04	0.11	5,390
73,000	0.11	8,030	11	1.50E-04	0.05	3,650
102,000	0.08	8,160	8	7.90E-05	0.03	3,060
122,000	0.06	7,320	6	4.90E-05	0.02	2,440
146,000	0.04	5,840	4	2.80E-05	0.01	1,460
				3.10E-03		

$M_w = \Sigma w_xM_x = 51{,}760$
$M_n = \Sigma \underline{N}_xM_x = 32{,}300$



5. Since amidation does not require a catalyst the polymerization rate is first order in both carboxyl and amine groups

$$-d[COOH] = k[COOH][NH_2]$$

For the stoichiometric reaction, where the carboxyl and amine group concentrations are the same (and symbolized by [M]), we have

$$-d[M]/dt = k[M]^2$$

which yields

$$1/[M] = kt + 1/[M]_0$$

on integration. This is the same kinetic expression as that obtained in Section 2-2b.

For the non-stoichiometric reaction, one obtains (see Section 2-6c of Odian book)

$$\ln([B]/[A]) = -\ln r + [B]_0(1-r)kt$$

where B is the functional group present in deficient amount.

6. $M_n = 21.3g/2.50 \times 10^{-3}$ mol $= 8.52 \times 10^3$ g/mol

This calculation assumes that each polymer molecule contains one COOH end group, i.e., the numbers of COOH and NH_2 end groups are equal. One can determine the validity of this assumption by experimentally determining the amounts of each of the end groups. The moles of polymer molecules can then be correctly taken to be one half of the total moles of both end groups.

These conclusions assume that the polyamide is synthesized from the diamine and diacid without the inclusion of a monofunctional reagent. If a monofunctional reagent is present, the end group analysis has to account for the appropriate end groups. For example, in a reaction system with of diacid, diamine, and ΦCOOH, end group analysis involves analysis of COOH, NH_2 and Φ end groups. The moles of polymer molecules is one half of the total moles of all three end groups.

7. a) For closed system

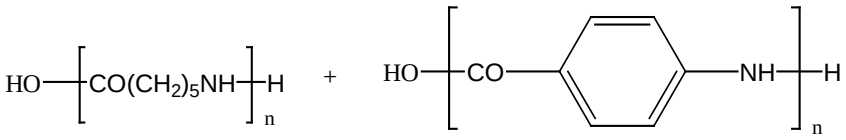
$p = K^{1/2}/(1+ K^{1/2}) = 14.14/(1+ 14.14) = 0.934$
$X_n = 1+ K^{1/2} = 15.1$

b) For open system

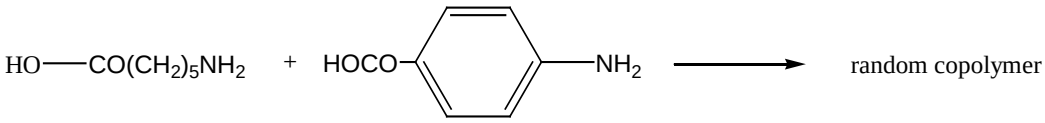
$[H_2O] = KM_0/ X_n(X_n-1) = 200(2)/200(199) = 1.00 \times 10^{-2}M$

8.

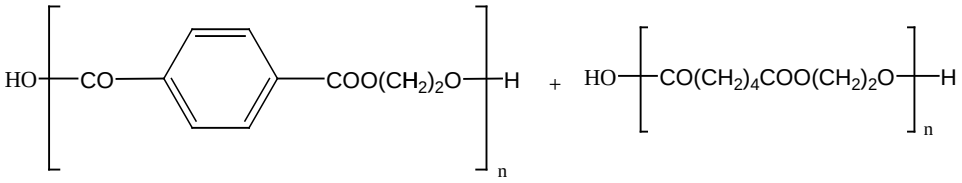
a)



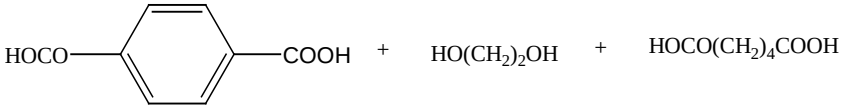
Block Copolymer



b)



block copolymer



random copolymer

9. (I)

a). $\overline{M}_n = \frac{\sum N_x M_x}{\sum N_x}$

$\sum N_x$ = Total number of moles = 2.71×10^{-4}

$\sum N_x M_x = (1.50 \times 10^{-5})(20{,}000) + (2.25 \times 10^{-5})(40{,}000) + \ldots + (5.63 \times 10^{-6})(160{,}000)$
$= 23.1$ g

$\overline{M}_n = (23.1\text{ g}) / (2.71 \times 10^{-4}\text{ mol}) = 8.52 \times 10^4$ g/mol

b). $\overline{M}_w = \frac{\sum N_x M_x^2}{\sum N_x M_x}$

$\sum N_x M_x^2 = (1.50 \times 10^{-5})(20{,}000)^2 + (2.25 \times 10^{-5})(40{,}000)^2 + \ldots + (5.63 \times 10^{-6})(160{,}000)^2$
$= 2.23 \times 10^6$ g^2/mol

$\sum N_x M_x = 23.1$ g

$\overline{M}_w = (2.23 \times 10^6\text{ g}^2/\text{mol}) / (23.1\text{ g}) = 9.65 \times 10^4$ g/mol

c). PDI = $\frac{\overline{M}_w}{\overline{M}_n} = (9.65 \times 10^4)/(8.52 \times 10^4) = 1.13$

(II)

a). The total number of moles is therefore equal to the number of fractions, 8.

$\sum N_x M_x = (1)(20{,}000) + (1)(40{,}000) + \ldots + (1)(160{,}000) = 720{,}000$ g

$\overline{M}_n = (720{,}000\text{ g}) / (8\text{ mol}) = 9.00 \times 10^4$ g/mol

b). $\sum N_x M_x^2 = (1)(20{,}000)^2 + (1)(40{,}000)^2 + \ldots + (1)(160{,}000)^2 =$
$= 8.16 \times 10^{10}$ g^2/mol

$\overline{M}_w = (8.16 \times 10^{10}\text{ g}^2/\text{mol}) / (720{,}000\text{ g}) = 1.13 \times 10^5$ g/mol

c). PDI = $\frac{\overline{M}_w}{\overline{M}_n} = (1.13 \times 10^5)/(9.00 \times 10^4) = 1.26$