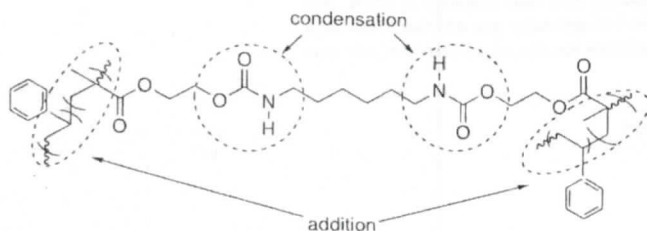


Solutions for Problem Set 2

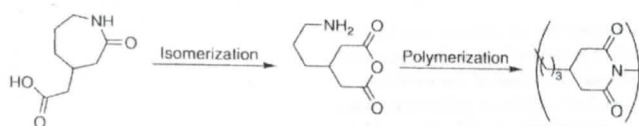
2. Haward et al. have reported some research in which a copolymer of styrene and hydroxyethylmethacrylate was cross-linked by hexamethylene di-isocyanate.¹ Draw the structural formula for a portion of this cross-linked polymer and indicate what part of the molecule is the result of a condensation reaction and what part results from addition polymerization. These authors indicate that the cross-linking reaction is carried out in sufficiently dilute solutions of copolymer that the cross-linking is primarily intramolecular rather than intermolecular. Explain the distinction between these two terms and why concentration affects the relative amounts of each.

2.2



Intramolecular crosslinking involves formation of urethane bridges between different hydroxyl groups of the same copolymer molecules. By contrast, intermolecular crosslinking results from the reaction of different molecules. The role of dilution arises from the fact that functional groups must come together in order to react. Reaction at high dilution increases the probability of intramolecular reactions compared to interchain crosslinks.

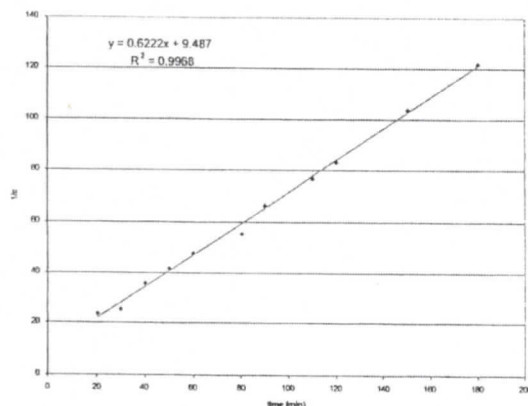
- 3.) The polymerization of β -carboxymethyl caprolactam has been observed to consist of initial isomerization via a second-order kinetic process followed by condensation of the isomer to polymer:



The rates of polymerization are thus of first order in ν_{NH_2} and in $\nu_{(\text{CO})_2\text{O}}$ or second order overall. Since $\nu_{\text{NH}_2} = \nu_{(\text{CO})_2\text{O}}$, the rate $= kc^2$, if catalyzed; third order is expected under uncatalyzed conditions. The indirect evaluation of c was accomplished by measuring the amount of monomer reacted, and the average degree of polymerization of the mixture was determined by viscosity at different times. The following data were obtained at 270°C ; the early part of the experiment gives nonlinear results.¹ Graphically test whether these data indicate catalyzed or uncatalyzed conditions, and evaluate the rate of constant for polymerization at 270°C . Propose a name for the polymer.

t (min)	c (Mole fraction)	t (min)	c (Mole fraction)
20	0.042	90	0.015
30	0.039	110	0.013
40	0.028	120	0.012
50	0.024	150	0.0096
60	0.021	180	0.0082
80	0.018		

- 2.3. Prepare two plots and look for linearity.



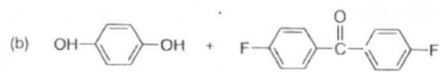
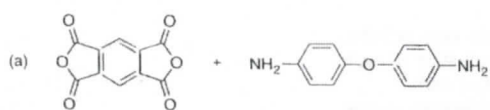
- (a) Plot c^{-1} vs t ; slope $= k_c$ if catalyzed, second order.

- (b) Plot c^{-2} vs t ; slope $= 2k_u$ if uncatalyzed, third order.

$t(\text{min})$:	20	30	40	50	60	80	90	110	120	150	180
c^{-1} :	24	26	36	42	48	56	67	77	83	104	122
c^{-2} :	568	657	1276	1736	2268	3086	4444	5917	6944	10850	14870

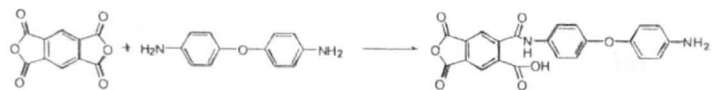
Second order plot considerably more linear than third order. Slope of second order plot $= k_c = 0.63 \text{ min}^{-1}$. IUPAC name: poly[(2,6-dioxo-1,4-piperidinediyl) trimethylene]

12. Show the reaction sequence and the structure of the resulting polymer from the polycondensation of these two monomers; note that the reaction (a) has two distinct steps, and that (b) it is base-catalyzed.

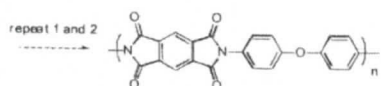
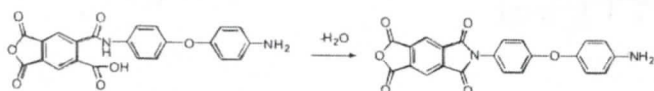


2.12(a)

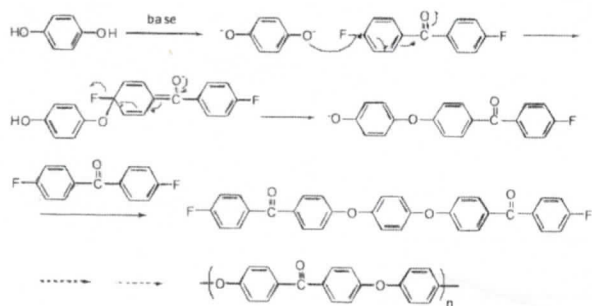
Step 1 Substitution



Step 2 Condensation



(b)



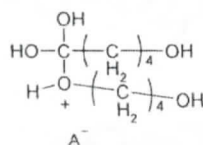
15. For the polymerization of succinic acid and 1,4-butanediol under stoichiometric balance in xylene:

- Draw the chemical structures of the reactants, products, and important intermediates for both the strong acid-catalyzed and self-catalyzed case.
- Generate a quantitative plot of N_n versus time for the self-catalyzed case up to 28,000 s, given $k = 6 \times 10^{-3} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-2}$ and 3 mol L^{-1} starting concentration of each monomer. How many hours would it take to make a polymer with $N_n = 300$?
- Do the same for the catalyzed case, with $k = 6 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$ and the same starting concentration. How many hours would it take to make a polymer with $N_n = 300$?
- Qualitatively explain the origin of the different shapes of the curves in the two plots.

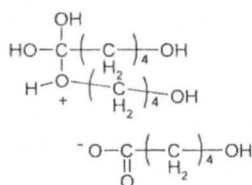
2.15(a)



Acid-catalyzed intermediate:

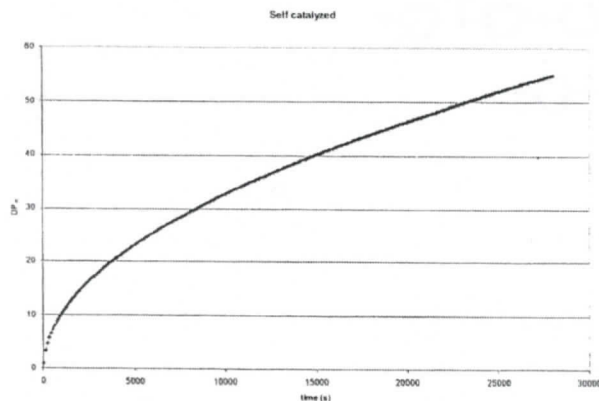


Self-catalyzed intermediate:



(b) For self-catalyzed:

$$DP_n^2 = 1 + 2[A]_0^2 kt$$

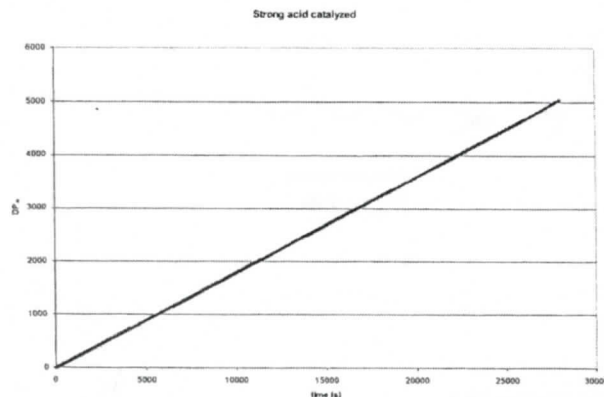


It would take 231.5 hours to obtain a number average degree of polymerization of 300

15 (cont.)

(c) For acid catalyzed:

$$N = 1 + [A]_0 kt$$

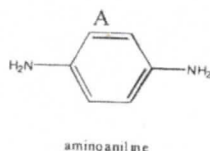


It would only take 0.5 hours to reach a number average degree of polymerization of 300.

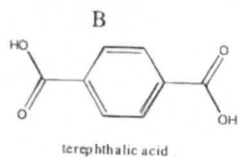
(d) In the self catalyzed reaction, catalyst is lost as monomer is consumed, resulting in a leveling off of the reaction. This effect is not observed for the strong acid catalyzed reaction.

16. Hydrolysis of an aromatic polyamide with $M_n = 24,116$ gives 39.31% by weight *m*-aminoaniline, 59.81% terephthalic acid, and 0.88% benzoic acid. Draw the repeat unit structure of the polymer. Calculate the degree of polymerization and the extent of reaction. Calculate what the degree of polymerization would have been if the amount of benzoic acid were doubled.

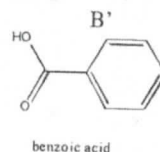
2.16



$$\begin{aligned} M_A &= 108 \\ \text{Wt}\% &= 39.31\% \\ N_A &= 50.461 \end{aligned}$$



$$\begin{aligned} M_B &= 166 \\ \text{wt}\% &= 59.81 \\ N_B &= 49.951 \end{aligned}$$



$$\begin{aligned} M_{B'} &= 122 \\ \text{wt}\% &= 0.88\% \\ N_{B'} &= 1 \end{aligned}$$

Neglecting the endgroups, $M_n = 24116$; d.p. = $M_n / ((M_A + M_B - 36)/2) = 202.42$

$$r = \frac{v_A}{v_B + 2v_{B'}} = \frac{50.461 \cdot 2}{49.951 \cdot 2 + 2} = 0.9904$$

$$N_n = \frac{1+r}{1+r-2rp}$$

$$202.42 = \frac{1+0.9904}{1+0.9904-2 \cdot 0.9904 \cdot p}$$

$$p = 0.99989$$

If the benzoic acid were doubled

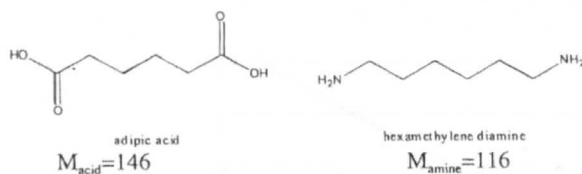
$$r = \frac{v_A}{v_B + 2v_{B'}} = \frac{50.461 \cdot 2}{49.951 \cdot 2 + 4} = 0.9713$$

$$p = 0.99988$$

$$N_n = 68.2$$

17. Calculate the feed ratio of adipic acid and hexamethylene diamine necessary to achieve a molecular weight of approximately 10,000 at 99.5% conversion. What would the identity of the end groups be in the resulting polymer?

2.17



For stoichiometric balance

$$N_n = \frac{1+r}{1+r-2rp}$$

$$p = 0.995 \quad N_n = 10000 / ((146 + 116 - 36) / 2) = 88.5$$

$$r = 0.9874$$

If $p_A = 0.995$, $p_B = r p = 0.9824$ (the choice of "A" and "B" is arbitrary)
The end groups are acids or amines, and the ratio is 1.013(0.995:0.9824).