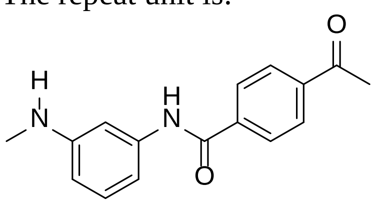
Problem Set 2 Solutions

2-1. a) Consider a 100g sample of polymer and convert % composition to mole composition.

Mol m-$H_2N\Phi NH_2$ = 39.31g/108.12gmol^{-1} = 0.3636
Mol p-$HO_2C\Phi CO_2H$ = 59.81/166.14 = 0.3600
Mol ΦCO_2H = 0.88/122.13 = 0.007206
The repeat unit is:

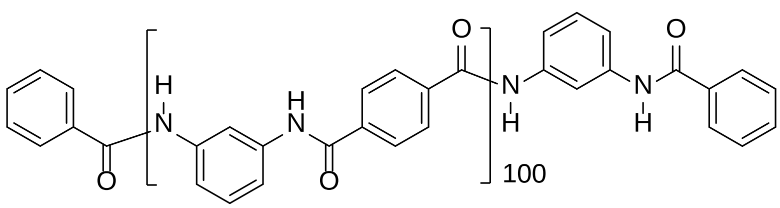


M_0 = one half of repeat unit = 238.22/2 = 119.11
X_n = 24,116/119.11 = 202.47

$r = N_A/(N_B + 2N_{B'})$ = 0.7272/(0.7200 + 0.014412) = 0.99018

$X_n = (1+r)/(1+r-2rp)$
202.47 = (1+0.99018)/[1+0.99018-2(0.99018)p]
p = 0.9999996 = 1.000

The formula of the polymer with X_n = 202.47 is



b) For 0.014412 moles ΦCO_2H:

r = (0.7272)/(0.7200 + 0.028824) = 0.9711

X_n at p = 1.00 = (1 + 0.9711)/[1 + 0.9711 – 2(0.9711)(1) = 68.20

2-2. M_0 = one half of MW of –NH$(CH_2)_6$ NHCO$(CH_2)_4$CO = 113
$X_n = M_n/ M_0$ = 15,000/113 = 132.7
$X_n = (1+r)/(1+r-2rp)$
For p = 0.995, X_n = 132.7
132.7 = (1+r)/[1+r-2r(0.995)]
r = 0.995

The polymerization is carried out with $COOH/NH_2$ or NH_2/ COOH = 0.995.

To calculate the identity of end groups, we need to calculate the number of unreacted COOH and NH_2. Consider the case of $COOH/NH_2$ = 0.995. The number of unreacted COOH groups is 0.995(1-p), which for p = 0.995 is 0.004975. The number of unreacted NH_2 groups is 0.004975 plus the excess of NH_2 over COOH, i.e., 0.004975 + 0.005 or 0.009975. The ratio of unreacted groups $COOH/NH_2$ is 0.004975:0.009975 or 1:2. Two thirds of the end groups are NH_2, one third is COOH. Note that if the reaction were carried out to 100% conversion, the only end groups would be NH_2. If the conversion were less than 99.5%, NH_2 end groups would constitute less than two-thirds of all end groups.

For M_n = 19,000, X_n = 168.1
r = 0.998

2-3. For M_n = 10,000, X_n = 10,000/113 = 88.5
r = 0.988 = $N_A/(N_B + 2N_{B'})$
Since $N_A = N_B = 1$, $N_{B'}$ = 0.00607
Therefore, use a molar ratio of 1:1:0.01214 of adipic acid:hexamethylene diamine:benzoic acid.

For M_n = 19,000, r = 0.995
$N_A = N_B = 1$, $N_{B'}$ = 0.00251
Use 1:1:0.00502 molar ratio of reactants

For M_n = 28,000, X_n = 247.8, one cacluates r to be greater than unity. This means that a degree of polymerization of 247.8 cannot be achieved for p = 0.995.

2-4. a) Consider 2 moles glycerol: 3 moles phthalic anhydride
Carothers: $f_{avg} = \Sigma N_i f_i / \Sigma N_i$ = [2(3) + 3(2)]/5 = 2.40
$p_c = 2/ f_{avg}$ = 2/2.40 = 0.833

b) 1.500 moles phthalic acid: 0.980 moles glycerol
Carothers: glycerol is not in excess
f_{avg} =2(0.980)(3)/(1.500 + 0.980) = 2.369
p_c = 2/2.369 = 0.844
c) 1.500 phthalic anhydride:0.990 glycerol:0.002 ethylene glycol

Carothers:

$f_{avg} = [2(N_A f_A + N_C f_C)/(N_A + N_C + N_B) =$

$[2(0.002(2) + 0.990(3))]/(0.002+0.990+1.500) = 2.39$

$p_c = 2/2.39 = 0.836$

d) 1.500 phthalic anhydride:0.500glycerol:0.700 ethylene glycol

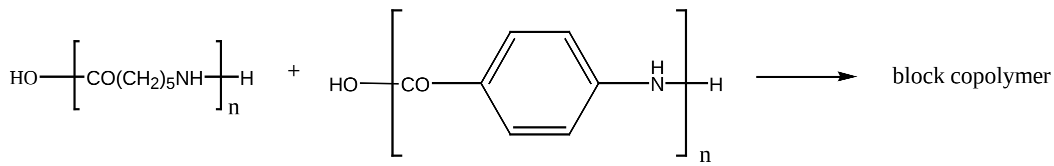
Carothers:

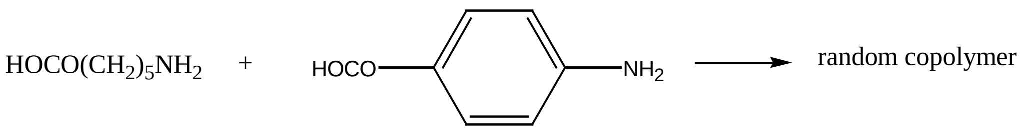
$f_{avg} = [2(0.700(2) + 0.500(3))]/(0.700+0.500+1.500) = 2.148$

$p_c = 2/2.148 = 0.93$

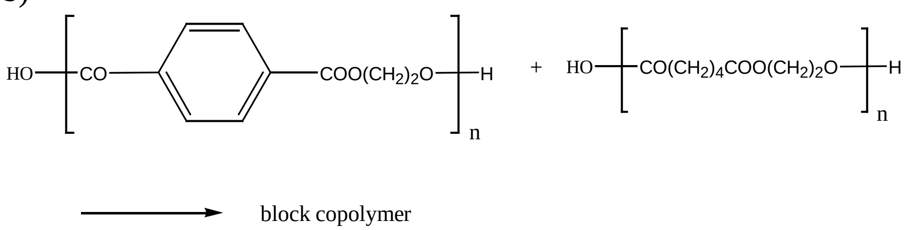
2-5

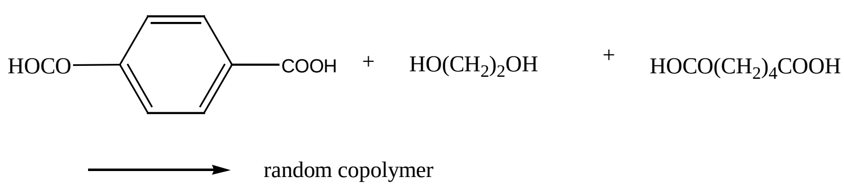
a)



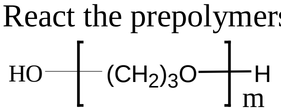


b)





2-6. React the prepolymers



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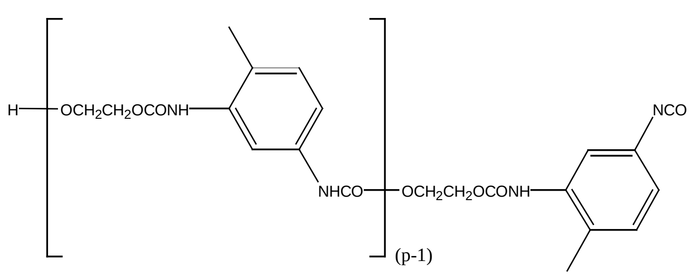


2-7. $M_n = X_n \times 104 \text{gmol}^{-1}$ styrene $= 1.52\times10^4 \times 104 \text{ gmol}^{-1}$ styrene
$= 1.58 \times 10^6 \text{ gmol}^{-1}$

(203 counts min^{-1}/3.22g)/9.81×10^7 counts $\text{mol}^{-1}\ \text{min}^{-1}$ =
6.43×10^{-7} mol AIBN per 1g polystyrene

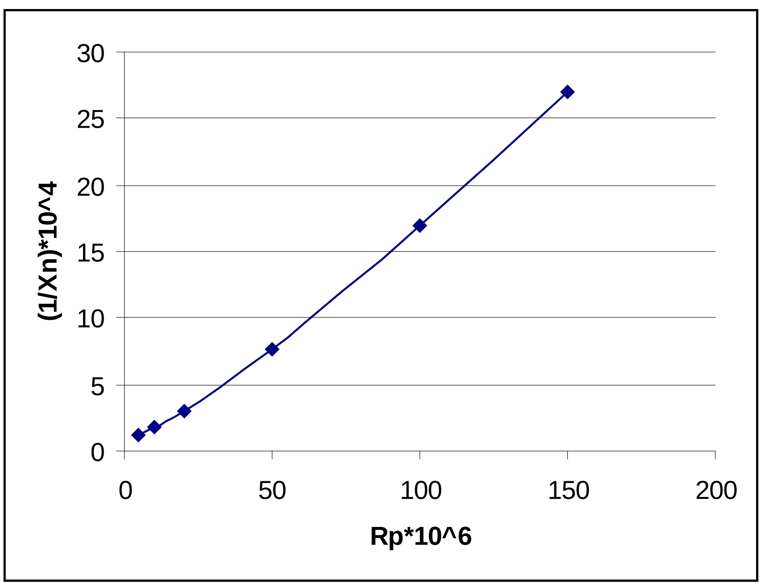
(1.0g)/$1.58\times10^6 \text{ gmol}^{-1} = 6.33*10^{-7}$ mol polystyrene per 1g polystyrene

This means that, within a precision of 1-2%, there is one molecule of AIBN or two initiator fragments (i.e., end groups) per polystyrene molecule. In other words, termination is exclusively by coupling.

2-8 Plot $(1/X_n)$ vs. R_p according to

$1/X_n = (k_t R_p)/(k_p^2 [M]^2) + C_M + C_I[I]/[M]$

Rp*10^6	Xn	(1/Xn)*10^4
5	8350	1.2
10	5550	1.8
20	3330	3
50	1317	7.6
100	592	16.9
150	458	27



The plot is linear at low R_p (i.e., the first three points). C_M = intercept = $5.97*10^{-5}$.

Slope = $k_t/(k_p^2 [M]^2 = 12.6$

$k_p^2 / k_t = 1/[1.26 \times 10^{-2}(8.3)^2 = 1.15 \times 10^{-3}$

$k_p / k_t^{1/2} = (1.15 \times 10^{-3})^{1/2} = 3.4 \times 10^{-2} L^{1/2}\, mol^{-1/2} s^{-1/2}$

$R_p = (k_p[M] / k_t^{1/2})(f\, k_d[I]^{1/2} = 4.0 \times 10^{-4}[I]^{1/2}$

$f\, k_d = ([4.0 \times 10^{-4}]/ k_p / k_t^{1/2}[M])^2 = ([4.0 \times 10^{-4}]/3.4 \times 10^{-2}(8.3))^2$
$= 2.0 \times 10^{-6}\, s^{-1}$

Transfer to initiator isimportant since the $1/X_n$ vs. R_p plot is not linear at higher R_p values. The C_I value can be obtained from the slope of the plot $[(1/X_n) - C_M](1/R_p)$ vs. R_p.