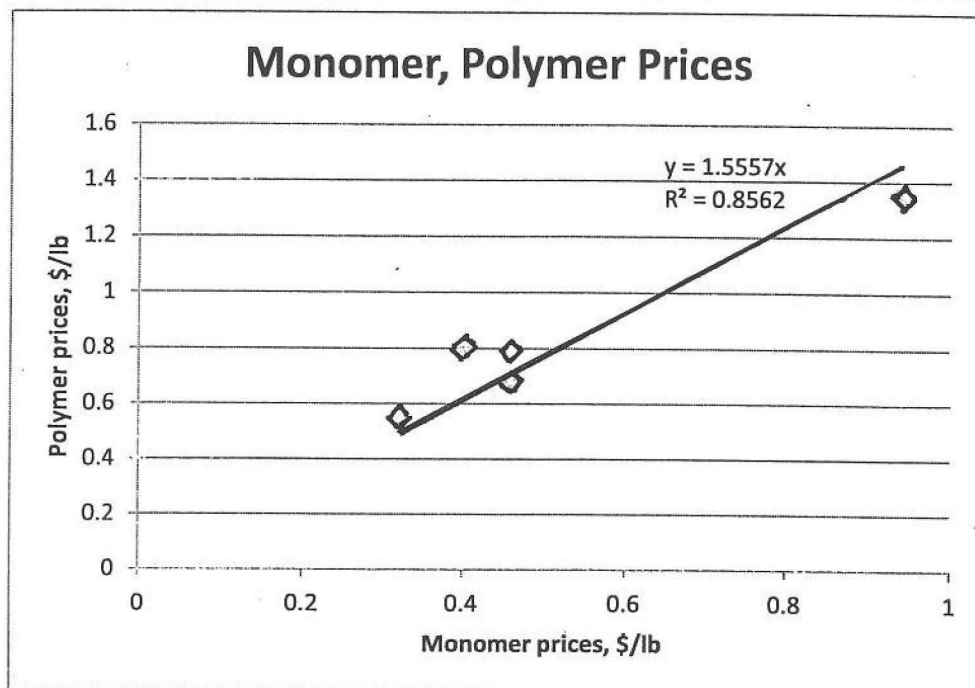


1-8

Chemical Marketing Reporter (Rebranded as ICIS)				
<a href="http://www.icis.com/chemicals/channel-info-chemicals-a-z/">http://www.icis.com/chemicals/channel-info-chemicals-a-z/</a>				
Monomer	Monomer Price	Polymer	Polymer Price	Polymer/Monomer
	\$/lb		\$/lb	
Ethylene	0.46	LLDPE	0.79	1.717391304
Propylene	0.46	PP	0.68	1.47826087
Styrene	0.4	PS	0.8	2
Vinyl chloride	0.32	PVC	0.55	1.71875
Bisphenol A	0.94	PC	1.35	1.436170213



## Chapter 2

2-1

$$\begin{aligned}
 \text{Mol. Wt. (100 \AA)} &= (\text{weight/molecule}) \times 6.02 \times 10^{23} \\
 &= (\pi D^3 \rho / 6) \times 6.02 \times 10^{23} \\
 &= \underline{3.15 \times 10^5} \text{ g/g-mole}
 \end{aligned}$$

$$\text{Mol. Wt. (1 micron)} = \text{Mol. Wt. (100 \AA)} \times 10^6 = \underline{3.15 \times 10^{11}} \text{ g/g-mole}$$

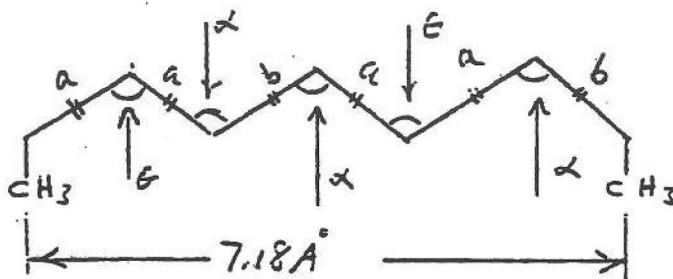
$$\text{Mol. Wt. (1 cm)} = \text{Mol. Wt. (100 \AA)} \times 10^{18} = \underline{3.15 \times 10^{23}} \text{ g/g-mole}$$

2-2 Possible stereoisomers are:

- a) cis, trans, mixture (because of double bond)
- b) isotactic, syndiotactic, atactic (because of -CHCl- group). However, because of distance between -CHCl- groups tacticity is unlikely to influence ability to crystallize unless rest of groups are all cis or trans.

Use 1.43 Å for C-O = a      108° for C-O-C =  $\theta$   
 1.54 " " C-C = b      110° for C-C-O =  $\alpha$

2-3 Graphical solution is easiest using protractor and ruler. Vector summation can be used, also.



If by syndiotactic we mean a succession of d and l monomer units, the distance turns out to be the same. Another structure is possible with methyls alternating so that the repeat distance would be doubled.

2-4 Refer to Table 2-4, Fig. 2-4.  
 Polyisobutylene in cyclohexane:

$$\chi = 0.436, \quad V_1 = 108, \quad v_2 = 0.10$$

$$NV_1 = 2.45 \times 10^{-3}, \quad \text{so that } N = 2.27 \times 10^{-5} \text{ mole/cm}^3$$

Same in toluene:

$$\chi = 0.557, \quad V_1 = 106, \quad NV_1 = 2.40 \times 10^{-3}, \quad \text{then } v_2 = 0.21$$

ie., swells to 4.75 x original volume.

2-5  $N = \rho/M$ , moles/volume = (g/vol)/(g/mole)

If  $M_0$  = Mol.Wt. per repeat unit = 58 for  $C_3H_6O$  (3 chain atoms)

then  $M_c$  = Mol.Wt. between cross-links =  $\frac{5000 \times 58}{3}$  g/mole

$$N = \frac{1.20 \times 3}{5000 \times 58} = 1.24 \times 10^{-5} \text{ mole/cm}^3$$

$$NV_1 = 102 \times 1.24 \times 10^{-5} / 0.800 = 1.58 \times 10^{-3}$$

From Fig. 2-4:  $v_2 = 0.069$

Assume additive volumes. Basis: Total volume = 1  $\text{cm}^3$

$$1.0 \text{ cm}^3 = v = v_1 + v_2 = 0.931 + 0.069$$

2-5 (cont'd):

$$\begin{aligned} \text{total weight/cm}^3 &= 0.931 \times 0.80 + 0.069 \times 1.2 = 0.745 + 0.083 \\ &= 0.828 \text{ g/cm}^3 \text{ (sample density)} \end{aligned}$$

2-6 Let  $y$  = dose,  $R$  = cross-link density of lowest dose,  
 $(N/2) = yR$ ,  $y = 1, 2, 4, 8, 16$

Substitute in Eq. 2-5:

$$-2yRV_1(v_2^{1/3} - v_2/2) = \ln(1-v_2) + v_2 + v_2^2 \chi$$

Rearrange to

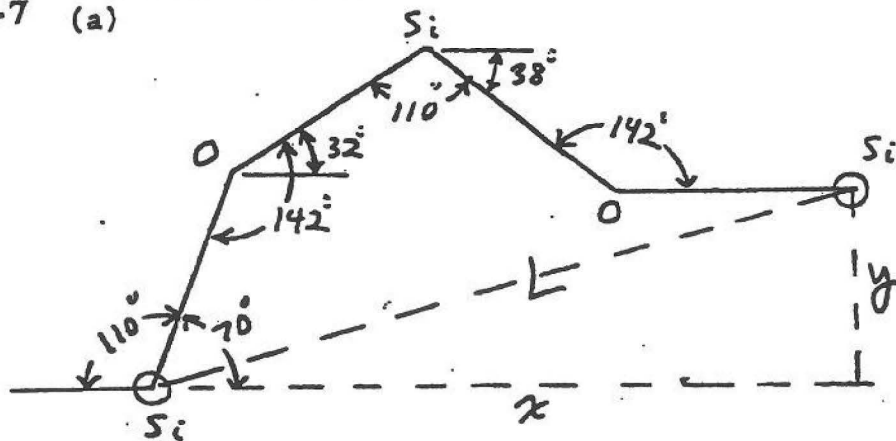
$$Y = 2RV_1X + \chi$$

where  $Y = (\ln(1-v_2) + v_2)/v_2^2$  and  $X = y(v_2^{1/3} - v_2/2)/v_2^2$

See plot (p. 7). Intercept gives  $\chi = 0.49$ , slope gives  
 $2RV_1 = 6.5 \times 10^{-4}$

Therefore,  $(N/2)_{16} = 4 \times 10^{-5} \text{ mole/cm}^3$ .

2-7 (a)



$$x = 1.64(\cos 70^\circ + \cos 32^\circ + \cos 38^\circ + \cos 0^\circ) = 1.64 \times 2.978$$

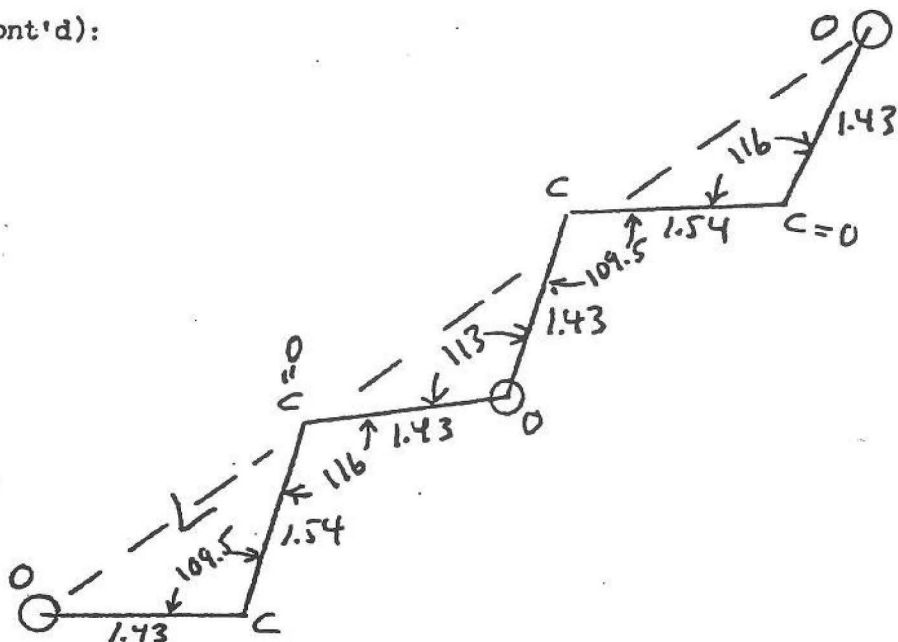
$$y = 1.64(\sin 70^\circ + \sin 32^\circ - \sin 38^\circ) = 1.64 \times 0.854$$

$$L = 1.64 \times 3.098 = 5.080 \text{ \AA/2 units, so for 1000 units,}$$

$$\Sigma L = 2,540 \text{ \AA or } \underline{\underline{254 \text{ nm}}}.$$

2-7 (cont'd):

(b)



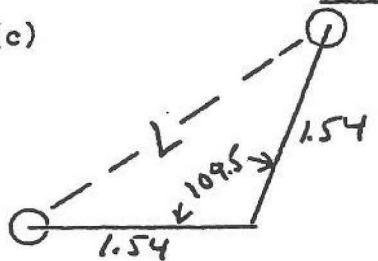
$$x = 1.54(\cos 70.5^\circ + \cos 3^\circ) + 1.43(\cos 0^\circ + \cos 6.5^\circ + \cos 73.5^\circ + \cos 67^\circ)$$

$$y = 1.54(\sin 70.5^\circ + \sin 3^\circ) + 1.43(\sin 6.5^\circ + \sin 73.5^\circ + \sin 67^\circ)$$

$$x = 5.87, \quad y = 4.38, \quad L = 7.32/2 \text{ units}$$

$$\text{For 1000 units, } \Sigma L = \underline{\underline{366 \text{ nm}}}$$

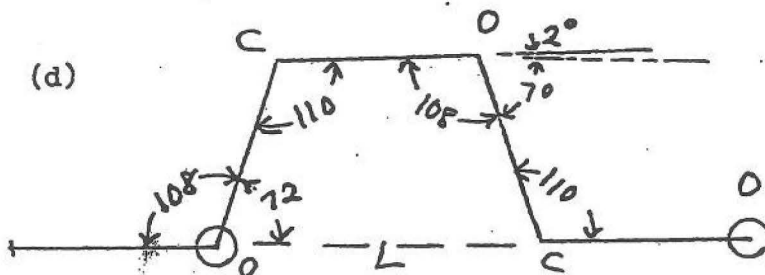
(c)



$$L = 2 \times 1.54 \times \cos 35.25^\circ = 2.52 \text{ \AA}$$

$$\text{For 1000 units, } \Sigma L = \underline{\underline{252 \text{ nm}}}$$

(d)

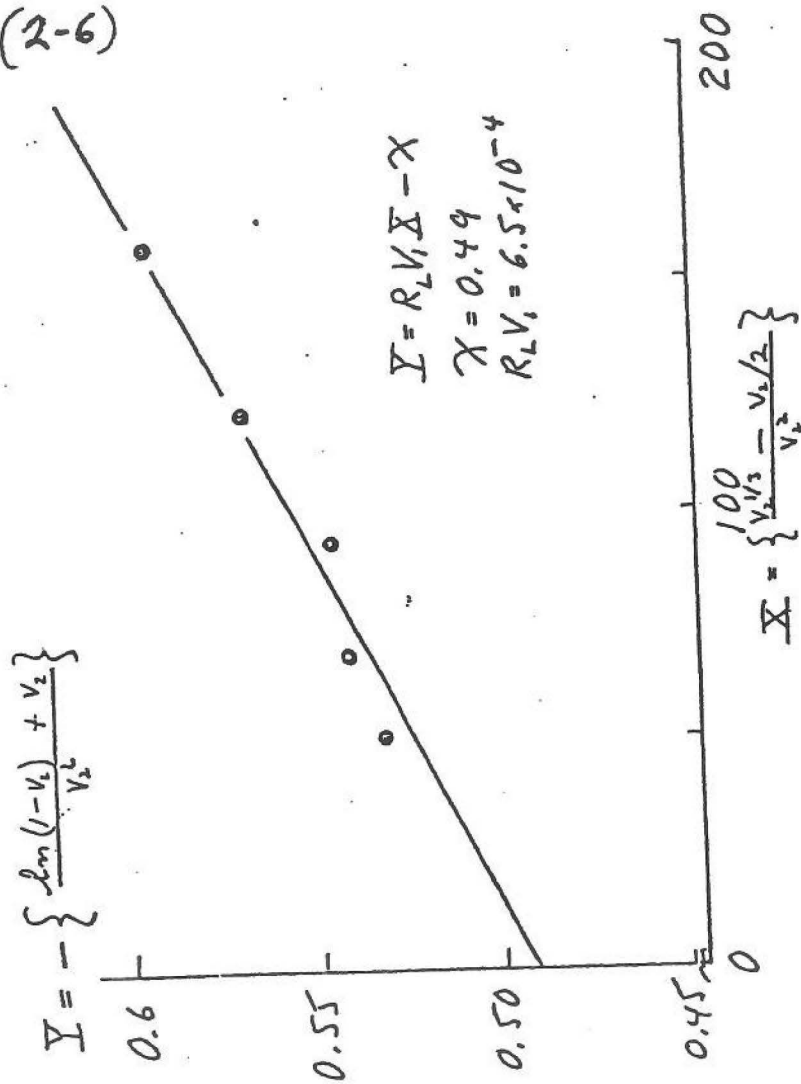


$$x = 1.43(\cos 72^\circ + \cos 2^\circ + \cos 70^\circ + \cos 0^\circ) = 3.790 \text{ \AA}$$

$$y = 1.43(\sin 72^\circ + \sin 2^\circ - \sin 70^\circ) = 0.066 \text{ \AA}$$

$$L = 3.79 \text{ \AA}/2 \text{ units, For 1000 units, } \Sigma L = \underline{\underline{189.5 \text{ nm}}}$$

(2-6)



$$Y = R_L V_1 X - X$$

$$X = 0.49$$

$$R_L V_1 = 6.5 \times 10^{-4}$$

- 2-8 a) In planar, zig-zag form, repeat distance is about 0.25 nm for every two chain atoms. Molecular weight per two chain atoms is 42.

$$\text{Length} = \frac{2 \times 10^6}{42} \times 0.25 \times 10^{-9} \text{ cm} = \underline{1.2 \times 10^{-3} \text{ cm}}$$

b)

$$\begin{aligned} \text{Volume} &= \frac{2 \times 10^6 \text{ g}}{6.023 \times 10^{23} \text{ molecule}} \times \frac{1 \text{ cm}^3}{0.906 \text{ g}} = 0.37 \times 10^{-17} \text{ cm}^3 \\ &= \underline{3.7 \times 10^{-3} \text{ nm}^3} = 3.7 \times 10^6 \text{ \AA}^3 \end{aligned}$$

2-9  $N = 2 \times (0.1 \text{ mol})/1000 \text{ cm}^3 = 0.2 \times 10^{-3} \text{ mol/cm}^3$

$$NV_1 = N \times 92.14 \text{ g/mol} / 0.867 \text{ g/cm}^3 = 0.00212$$

$$v_2 = 1/4.35 = 0.23$$

$$\ln(0.77) + 0.23 + \chi(0.23)^2 = -0.00212 \{ (0.23)^{1/3} - 0.23/2 \}$$

$$-0.003136 + \chi(0.23)^2 = -0.001055 \text{ So } \chi = 0.002081/(0.23)^2 = 0.393$$

$$[\text{Nomograph gives } \chi = 0.41]$$

$$\text{New value of } v_2 = 1/3.45 = 0.29$$

$$\text{Using } \chi = 0.39 \text{ gives } NV_1 = 0.0039$$

$$\text{Using } \chi = 0.41 \text{ gives } NV_1 = 0.0037$$

$$\text{Thus } N/2 = (NV_1/2) \times (0.867/92.14) = 1.83 \times 10^{-4} \text{ crosslinks/cm}^3$$

$$\text{Also Amount of sulfur} = (28 \times 10^{-3} / 32) = 0.875 \times 10^{-3} \text{ mols of S/cm}^3$$

Therefore, each crosslink contains an equal amount of sulfur

$$\text{The amount of sulfur in each crosslink is } = 0.875 \times 10^{-3} / 1.83 \times 10^{-4} = \underline{4.78 \text{ S/crosslink}}$$

## 2-10

Case I: Concentration of 0.020 g A/100 g P =  $c_1$

$$v_2 = 5/75 = 0.067$$

$$\chi = \beta + (V_1/RT)(\delta_1 - \delta_2)^2 \quad \text{and so } \chi = \beta = 0.475$$

Therefore  $(NV_1)_I = 5.8 \times 10^{-4}$  from equation 2-5 using  $v_2$  and  $\chi$ .

Case II: Concentration =  $c_2$

$$\text{We want } v_2 = 5/25 = 0.200$$

$$(NV_1)_{II} = 0.85 \times 10^{-2} \text{ from equation 2-5 using new } v_2 \text{ and same } \chi.$$

Since  $V_1$  does not change, the concentrations used are just proportional to  $N$  or  $NV_1$ :

$$c_2/c_1 = (NV_1)_{II}/(NV_1)_I = 0.0085/0.00058 = 14.6$$

$$\text{Thus we need } 0.020 \times 14.6 = \underline{0.29 \text{ g of A/100 g P} = c_2}$$

## 2-11 In solvent A:

$$\chi_A = \beta_1 + (V_1/RT)(\delta_A - \delta_P)^2 \quad \text{so } \beta_1 = 0.33$$

$$\delta_P = (CED)^{1/2} = (85)^{1/2} = 9.22$$

From Fig. 2-4, if  $\chi_A = 0.33$  at  $v_2 = 0.1$ , then at  $v_2 = 0.2$ ,

$\chi_B$  must equal 0.52. That is,  $(NV_1) = 5.0 \times 10^{-3}$  in either solvent. Then  $\chi_B = \beta_1 + (V_1/RT)(\delta_B - \delta_P)^2$

$$\text{or } 0.52 = 0.33 + (100/600)(\delta_B - 9.22)^2$$

$\delta_B = 9.22 \pm 1.07 = 8.15 \text{ or } 10.29$ . But all lactones (Figure 2-6) have high solubility parameters, so lower value is ruled out.

$$\underline{\delta_B = 10.29 \text{ (cal/cm}^3)^{1/2}}$$

## 2-12 $N = 2C$ where $C$ = number of moles of crosslinks

$$\text{a) } C = [I] = \frac{(0.5/242) \times 0.97}{100} = 2.0 \times 10^{-5} \text{ moles/cm}^3$$

$$\underline{N = 4.0 \times 10^{-5} \text{ moles of chains/cm}^3}$$

$$\text{b) } NV_1 = 4.0 \times 89 \times 10^{-5} = 3.56 \times 10^{-3}, \quad \chi = 0.40$$

Figure 2-4 gives ( $a = 3$ )  $v_2 = 0.105$

$$\text{Swollen volume} = 1/v_2 = \underline{9.5 \text{ cm}^3}$$

$$2-13 \quad N = 1.00 \text{ mole}/(425 \times 78) \text{ cm}^3 = 3.017 \times 10^{-5} \text{ mole/cm}^3$$

$$V_1 = 114/0.703 = 162 \text{ cm}^3/\text{mole} \quad NV_1 = 4.89 \times 10^{-3}$$

$$\text{From Figure 2-4, } v_2 = 0.175. \quad \text{Swollen volume} = 1/v_2 = \underline{5.71 \text{ cm}^3}$$

## 2-14

$$\text{In S: } v_2 = 1/4.55 = 0.220 \text{ and } \chi = 0.5 \quad \text{so } NV_1 = 8.63 \times 10^{-3} \text{ (Eq. or graph)}$$

$$\text{In Q: } \delta Q = (29,900 \times 0.86/88.0)^{1/2} = 17.1 \text{ (MPa)}^{1/2}$$

$$\text{In Q: } \chi = 0.40 + (88.0/0.86)(1/300)(1/8.31)(17.1 - 16.0)^2 = 0.450$$

$$\text{New value of } (NV_1) \text{ in Q} = (NV_1) \text{ in S} \times \{V_1(Q)/V_1(S)\} = 8.63 \times 10^{-3} \times (88.0/0.86)/216$$

$$\text{So } f(NV_1) \text{ in Q} = 4.09 \times 10^{-3} \quad \text{and Eq. or graph gives } v_2 = 0.133 = 1/7.52$$

That is, the polymer swells in Q to 7.52 times its original (dry) volume.

## 2-15

$$\chi = 0.300 + [100/(2 \times 300)][7.00 - \delta_p]^2 = 0.300 + [100/(2 \times 300)][8.80 - \delta_p]^2$$

$$\text{So } \pm(7.00 - \delta_p) = 8.80 - \delta_p$$

$$\delta_p = (7.70 + 8.80)/2 = 15.80/2 = \underline{7.90}$$

$$\chi_A = \chi_B = 0.435 \quad \text{In A: } v_2 = 0.25$$

$$\text{So } NV_1 = 2.1 \times 10^{-2} \text{ (Using nomograph, Eq. gives } = 2.08 \times 10^{-2})$$

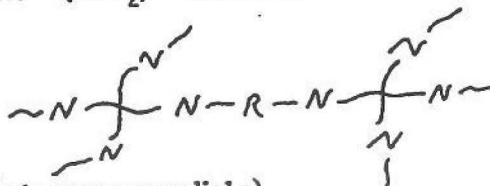
$$\text{In C: } (NV_1)_C = 2.5 (NV_1)_A = 5.2 \times 10^{-2}$$

$$\chi_C = 0.300 + \{250/(2 \times 300)\}(8.20 - 7.90)^2 = 0.3375$$

$$\text{Nomograph gives } v_2 = 0.30 \text{ so swollen volume} = (1/v_2) = 3.33 \text{ cm}^3$$

## 2-16

$$\chi = 0.43, \quad V_1 = 112.5/1.10 = 102 \text{ cm}^3/\text{mol}$$



There are 2 nitrogens's for each chain (each segment between crosslinks)

Concentration of chains = 0.5 x concentration of nitrogen

$$\text{Conc. of nitrogen} = (2.10 \text{ g/liter})/(14.0 \text{ g/mol of nitrogen}) = 0.15 \text{ mol/liter}$$

$$\text{Conc. of chains} = 0.15/2 = 0.075 \text{ mol/liter}$$

$$NV_1 = (0.075 \text{ mol/liter}) \times (102 \text{ cm}^3/\text{mol}) \times (\text{liter}/1000 \text{ cm}^3) = 7.65 \times 10^{-3}$$

$$\text{From equation or nomograph, } v_2 = 0.167 = 1/6.00$$

So 1 cm<sup>3</sup> swells to 6.00 cm<sup>3</sup>.



## 2-17

Each PE is a crosslink and corresponds to two chains:

$$200 \times 58 = 11,600$$

$$1 \times 136 = 136$$

$$2 \times 110 = 220$$

$$\text{Total} = 11,956 \text{ g} = 2 \text{ mols of chains}$$

$$N = (2 \text{ mols}/11,956 \text{ g}) \times 1.06 \text{ g/cm}^3 = 0.177 \times 10^{-3} \text{ mol/cm}^3$$

$$V_1 = (92.14 \text{ g/mol})/(0.862 \text{ g/cm}^3) = 106.9 \text{ cm}^3/\text{mol}$$

$$NV_1 = 18.9 \times 10^{-3}, \text{ and } v_2 = 1/3.57 = 0.280$$

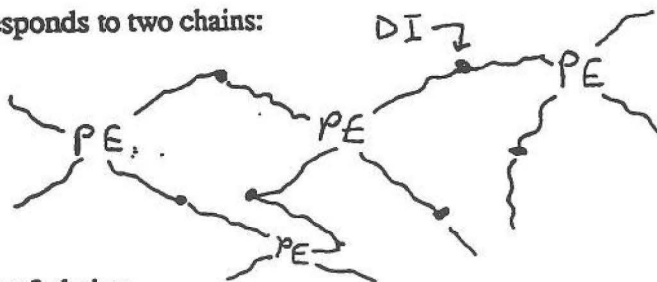
$$\chi \text{ (from nomograph or equation)} = 0.50 \text{ (actually 0.495 from equation)}$$

$$\chi = \beta + (V_1/RT)(\delta_1 - \delta_2)^2$$

$$0.495 = 0.300 + [106.9/(1.987 \times 300)][8.90 - \delta_2]^2$$

$$0.195 \times 5.576 = 1.087 = [8.90 - \delta_2]^2$$

$$\delta_2 = \underline{\underline{8.90 \pm 1.04}} \text{ (but 9.94 is more likely than 7.86 on basis of polarity.)}$$



## 2-18

$\chi = 0.48$  Calculate  $NV_1$  from equation 2-5 using known  $v_2$ :

"Doubly cross-linked"

$$v_2 = 10/55.6 = 0.180$$

$$(NV_1) = 6.11 \times 10^{-3}$$

"After hydrolysis"

$$v_2 = 10/83.3 = 0.120$$

$$(NV_1) = 2.13 \times 10^{-3}$$

Mols crosslinks/volume =  $N/2$  (One crosslink for each two chain segments)

$$\text{Covalent crosslinks/Total crosslinks} = 2.13/6.11 = 0.349$$

Therefore, ester bonds were  $1.000 - 0.349 = \underline{0.651}$  of original total.

## 2-19

$$\Delta G_{gel} = RT(\chi N_1 v_2 + N_1 \ln v_1) + (3/2)RT\zeta(v_2^{-2/3} - 1)$$

$$\left(\frac{\partial v_1}{\partial N_1}\right)_{T,N_2} = -\left(\frac{\partial v_2}{\partial N_1}\right)_{T,N_2} = \frac{v_1 v_2}{N_1} \quad \left(\frac{\partial v_1}{\partial N_1}\right)_{T,N_2} = -\left(\frac{\partial v_2}{\partial N_1}\right)_{T,N_2} = \frac{v_1 v_2}{N_1}$$

$$\left(\frac{\partial \Delta G_{gel}}{\partial N_1}\right)_{T,N_2} = RT \left[ \chi N_1 \left(\frac{\partial v_2}{\partial N_1}\right)_{T,N_2} + \chi v_2 + \ln v_1 + N_1 \frac{\left(\frac{\partial v_1}{\partial N_1}\right)_{T,N_2}}{v_1} + \frac{3}{2}\zeta \left(\frac{\partial v_2^{-2/3}}{\partial N_1}\right)_{T,N_2} \right] \quad (1)$$

Need to determine  $\left(\frac{\partial v_2}{\partial N_1}\right)_{T,N_2}$ ,  $\left(\frac{\partial v_1}{\partial N_1}\right)_{T,N_2}$ , and  $\left(\frac{\partial v_2^{-2/3}}{\partial N_1}\right)_{T,N_2}$ :

$$\left(\frac{\partial v_2}{\partial N_1}\right)_{T,N_2} = \frac{\partial}{\partial N_1} \left( \frac{V_p}{N_1 V_1 + V_p} \right) = - \left( \frac{V_1 V_p}{N_1 V_1 + V_p} \right) = -V_1 v_2 = -\frac{v_1 v_2}{N_1} \quad (2)$$

where  $V_p$  is the volume of dry polymer.

$$\text{Because of the assumption } v_1 + v_2 = 1, \quad \left(\frac{\partial v_1}{\partial N_1}\right)_{T,N_2} = -\left(\frac{\partial v_2}{\partial N_1}\right)_{T,N_2} = \frac{v_1 v_2}{N_1} \quad (3)$$

$$\text{Finally, } \left(\frac{\partial v_2^{-2/3}}{\partial N_1}\right)_{T,N_2} = -\frac{2}{3} v_2^{-5/3} \left(\frac{\partial v_2}{\partial N_1}\right)_{T,N_2} = \frac{2}{3} v_2^{-5/3} \left(\frac{\partial v_2}{\partial N_1}\right)_{T,N_2} = \frac{2}{3} \frac{v_1 v_2^{-2/3}}{N_1} = \frac{2}{3} \frac{V_1 v_2^{-2/3}}{V}$$

where  $V = N_1 V_1 + V_p$  = total volume (4)

Substitution of Eqs. (2) – (4) into Eq. (1) yields:

$$\begin{aligned} \left(\frac{\partial \Delta G_{gel}}{\partial N_1}\right)_{T,N_2} &= RT \left[ \chi v_2^2 + \ln(1 - v_2) + v_2 + N V_1 v_2^{1/3} \right] \\ &= RT \left[ -\chi v_1 v_2 + \chi v_2 + \ln(1 - v_2) + v_2 + \zeta \frac{V_1 v_2^{1/3}}{V_p} \right] \\ &= RT \left[ \chi v_2^2 + \ln(1 - v_2) + v_2 + N V_1 v_2^{1/3} \right] \end{aligned}$$

where  $N = \zeta/V_p$  is the density of elastic strands in the dry state.

At equilibrium,  $\left(\frac{\partial \Delta G_{gel}}{\partial N_1}\right)_{T,N_2} = \mu_1 - \mu_1^0 = 0$  and Eq. (2.17) of the text is recovered.

2-20

a)

$$\begin{aligned}\Omega_M &= \frac{1}{n_2!} \prod_{n_2=0}^{n_2-1} \frac{(z-1)^{x-1}}{n^{x-1}} (n - xn_2')^x \\ \Omega_M &= \frac{1}{n_2!} \frac{(z-1)^{n_2(x-1)}}{n^{n_2(x-1)}} \prod_{n_2=0}^{n_2-1} (n - xn_2')^x \\ \Omega_M &= \frac{x^{xn_2}}{n_2!} \left( \frac{z-1}{n} \right)^{n_2(x-1)} \prod_{n_2=0}^{n_2-1} \left( \frac{n}{x} - n_2' \right)^x\end{aligned}\quad (1)$$

But 
$$\prod_{n_2=0}^{n_2-1} \left( \frac{n}{x} - n_2' \right)^x = \left[ \left( \frac{n}{x} \right) \left( \frac{n}{x} - 1 \right) \left( \frac{n}{x} - 2 \right) \dots \left( \frac{n}{x} - n_2 + 1 \right) \right]^x$$

$$\prod_{n_2=0}^{n_2-1} \left( \frac{n}{x} - n_2' \right)^x = \left[ \frac{\left( \frac{n}{x} \right) \left( \frac{n}{x} - 1 \right) \left( \frac{n}{x} - 2 \right) \dots (3)(2)(1)}{\left( \frac{n}{x} - n_2 \right) \left( \frac{n}{x} - n_2 - 1 \right) \dots (3)(2)(1)} \right]^x$$

$$\prod_{n_2=0}^{n_2-1} \left( \frac{n}{x} - n_2' \right)^x = \left[ \frac{\left( \frac{n}{x} \right)!}{\left( \frac{n}{x} - n_2 \right)!} \right]^x$$

Substitution into Eq. (1) yields Eq. A2.7 of the text:

$$\Omega_M = \left( \frac{z-1}{n} \right)^{(x-1)n_2} \frac{x^{xn_2}}{n_2!} \left[ \frac{(n/x)!}{(n/x - n_2)!} \right]^x$$

## 2-20 (continued)

b) Taking the natural logarithm of the preceding equation, we get:

$$\ln \Omega_M = n_2(x-1)[\ln(z-1) - \ln n] + xn_2 \ln x - \ln n_2! + x[\ln(n/x)! - \ln(n/x - n_2)!]$$

Using Sterling's approximation:  $\ln n! \approx n \ln n - n$  and the fact that  $n = n_1 + xn_2$ , we get:

$$\ln \Omega_M = n_2(x-1)[\ln(z-1) - \ln n] + xn_2 \ln x - n_2 \ln n_2 + n_2 + x[\ln(n/x)! - \ln(n_1/x)!]$$

$$\ln \Omega_M = n_2(x-1)[\ln(z-1) - \ln n] + xn_2 \ln x - n_2 \ln n_2 + n_2 + x[(n/x)(\ln n - \ln x) - n/x - (n_1/x)(\ln n_1 - \ln x) + n_1/x]$$

Further algebraic simplifications using  $n = n_1 + xn_2$  give:

$$\ln \Omega_M = n_2(x-1)\ln(z-1) + n_2 \ln n - n_2 \ln n_2 - n_2(x-1)$$

that can be rewritten as:

$$\ln \Omega_M = -n_1 \ln(n_1/n) - n_2 \ln(n_2/n) + n_2(x-1)\ln(z-1) - n_2(x-1)$$

Finally, from  $S_M = k \ln \Omega_M$ , we recover Eq. (A2.9) of the text:

$$S_M = -k \left[ n_1 \ln \frac{n_1}{n_1 + xn_2} + n_2 \ln \frac{n_2}{n_1 + xn_2} \right] + k(x-1)n_2 [\ln(z-1) - 1]$$

## 2-21

From Eq. (A2.9), setting  $n_2 = 0$ , we get

$$S_1 = -k[n_1 \ln 1 + 0] + 0 = 0; \quad (1)$$

and for  $n_1 = 0$ , we get:

$$S_2 = -k[0 + n_2 \ln(1/x)] + k(x-1)n_2[\ln(z-1) - 1]. \quad (2)$$

Substitution of Eqs. (A2.9), (1) and (2) into:

$$\Delta S_M = S_M - S_1 - S_2 \quad \text{gives:}$$

$$\Delta S_M = -k \left[ n_1 \ln \frac{n_1}{n} + n_2 \ln \frac{n_2}{n} \right] + k(x-1)n_2 [\ln(z-1) - 1] - kn_2 \{ \ln(x) \} + (x-1) [\ln(z-1) - 1] \}.$$

$$\text{This can be rewritten as: } \Delta S_M = -k[n_1 \ln(n_1/n) + n_2 \ln(n_2x/n)] \quad (3)$$

Because  $x = V_2/V_1$ ,

$n_1/n = n_1/(n_1 + n_2x) = n_1 V_1/(n_1 V_1 + n_2 V_2) = v_1$ , and

$n_2x/n = n_2 V_2/(n_1 V_1 + n_2 V_2) = v_2$ .

Substitution in Eq. (3) gives the desired result:

$$\Delta S_M = -k(n_1 \ln v_1 + n_2 \ln v_2) = -R(N_1 \ln v_1 + N_2 \ln v_2).$$

## 2-22

Use the group contribution method formula:

$$\delta = \rho \sum F_i / \sum M_i$$

where  $\rho$ ,  $F_i$  and  $M_i$  are the density of the polymer, the attraction constant of group  $i$  and the molar mass of group  $i$ , respectively.

For PE, we get:

$$\delta_{PE} = 0.86 \text{ g/cm}^3 \times 135 \text{ cal}^{1/2} \text{ cm}^{3/2} / 14 \text{ g} = 8.29 \text{ cal}^{1/2} \text{ cm}^{-3/2} \\ \text{or } 16.97 \text{ (MPa)}^{1/2} \text{ approx.. 4.7\% from experimental value.}$$

For PVC, we get:

$$\delta_{PVC} = 1.39 \text{ g/cm}^3 \times (135+60+230) 135 \text{ cal}^{1/2} \text{ cm}^{3/2} / 62.48 \text{ g} \\ = 9.45 \text{ cal}^{1/2} \text{ cm}^{-3/2} \text{ or } 19.34 \text{ (MPa)}^{1/2} \\ \text{approx. 2.3 \% from experimental value.}$$