SOLUTIONS MANUAL FOR
PRINCIPLES OF
POLYMER SYSTEMS

SIXTH EDITION

Ferdinand Rodriguez
Claude Cohen
Christopher K. Ober
Lynden A. Archer

CRC Press
Taylor & Francis Group

SOLUTIONS MANUAL FOR
PRINCIPLES OF
POLYMER SYSTEMS

SIXTH EDITION

Ferdinand Rodriguez
Claude Cohen
Christopher K. Ober
Lynden A. Archer

CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2015 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works

Printed on acid-free paper
Version Date: 20141030

International Standard Book Number-13: 978-1-4822-2395-8 (Ancillary)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (http://www.copyright.com/) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Visit the Taylor & Francis Web site at
http://www.taylorandfrancis.com

and the CRC Press Web site at
http://www.crcpress.com

TABLE OF CONTENTS

SOLUTIONS TO PROBLEMS IN THE TEXT

Chapter 1

1-1 See also Mod. Plastics Encyclop., pp. A24 and A26, Nov., 1994.

Some uses include:

paints and coatings
flooring such as vinyl tile
wire covering (PVC, polyethylene, rubber)
pipe and fittings (a growing market as plastic pipe becomes acceptable)
adhesive and caulking
vapor barriers and insulation (polyethylene sheet)
plywood (phenolic adhesive) and siding (vinyl)
wall coverings
lighting fixtures
decorative laminates (kitchen countertops)
plumbing fixtures (metallized knobs, etc.)

1-2 See also Mod. Plastics Encyclop., p. A28, Nov., 1994.

Traditional uses include:

bushings and seals
gaskets
weather stripping
wire insulation
seat cushioning (urethane foam)
fender extensions (poly(oxymethylene))
safety glass interlayer (poly(vinyl butyral))
molded knobs, handles
hose
diaphragms
floor mats
tail light lenses (acrylic plastic)
dashboard cushioning
molded auto body (Chevrolet's Corvette, for example)

1-3 Cellulose-based paper:
readily oxidized
attacked by fungi
low tear strength

Polyethylene:
hard to print on permanently
low modulus
pigmentation needed for opacity
harder to recycle

According to Stat. Abstract of U.S., 1980, Table 1304, p. 758, consumption of newsprint in 1979 was $11.2\text{x}10^6$ tons (of 2000 lb/ton) and consumption of bookpaper in 1977 was $3.2\text{x}10^6$ tons.

1-4 For windshield assume a sheet $(4/3) \times 6 \times (1/48)\ \mathrm{ft}^3 = 1/6\ \mathrm{ft}^3$

Density (Table A5-1) = $1.2\ \mathrm{g/cm^3}$

$$\text{Total new consumption} = \left(10^7\ \frac{\text{cars}}{\text{yr}}\right)\left(1.2\ \frac{\text{g}}{\text{cm}^3}\right)\left(\frac{1\ \text{ft}^3}{6\ \text{car}}\right) \times 62.4\ \frac{\text{lb-cm}^3}{\text{ft}^3\text{-g}}$$

$$\text{" \quad " \quad "} = 1.25 \times 10^8\ \text{lb/yr}$$

Production in 1994 was 700×10^6 lbs so new total would be 825×10^6 lbs.

Assuming power dependence of price on volume:

New price = Old price $(700/825)^{0.4}$ = <u>0.94 x Old price.</u>

1-5 Factors include:

Raw material costs
Energy costs
Safety hazards and waste disposal costs
Number of steps in synthesis (for example: SiO_2 to Si to $SiCl_4$ to $SiMe_2Cl_2$ to $(SiMe_2O)_4$ to polymer)
Marketing or disposal of by-products (chlorinated alkanes and alkenes from vinyl chloride production)

1-6

	A.Acetal	B. Polypropylene
Typical density, g/cm^3	1.42	0.905
Price (2013/2014), $/lb	1.49	0.71

To compete, price of Acetal would have to be 0.64 the price Polypropylene. Ie. 0.905/1.42=0.64. Thus, Acetal would have to be priced at 0.64x0.71= $0.45/lb instead of the actual $1.49/lb.

1-7

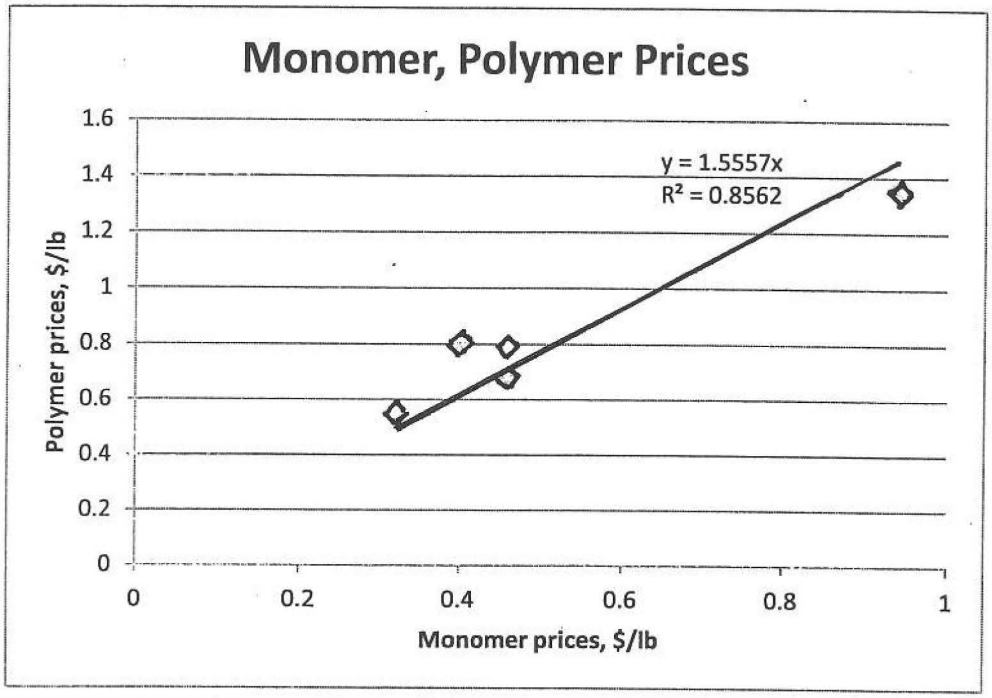
Approximate dependency on polymer cost:

Item	Typical $/item (2014)	lb polymer per item	Polymer cost $/item(2014)	Polymer cost %
PE Garbage Can	6.00	4	3.76	62.7
Automobile tire	75.00	15	15	20
Nylon pocket comb	2.00	0.10	0.18	9
Nylon panty hose	8.00	0.10	0.18	2.25
Tilted sunglasses (cellulose acetate)	20.00	0.05	0.09	0.45
Nylon guitar string	5.00	0.01	0.018	0.36

Other cost contributing factors: Other ingredients (tire), manufacturing/assembly (tire, glasses), packaging (string, panty hose), advertising (low on cans and combs), size of market (small for strings).

1-8

<table>
<tr><td colspan="6">Chemical Marketing Reporter (Rebranded as ICIS)</td></tr>
<tr><td colspan="6">http://www.icis.com/chemicals/channel-info-chemicals-a-z/</td></tr>
<tr><td>Monomer</td><td>Monomer Price</td><td>Polymer</td><td>Polymer Price</td><td>Polymer/Monomer</td></tr>
<tr><td></td><td>$/lb</td><td></td><td>$/lb</td><td></td></tr>
<tr><td>Ethylene</td><td>0.46</td><td>LLDPE</td><td>0.79</td><td>1.717391304</td></tr>
<tr><td>Propylene</td><td>0.46</td><td>PP</td><td>0.68</td><td>1.47826087</td></tr>
<tr><td>Styrene</td><td>0.4</td><td>PS</td><td>0.8</td><td>2</td></tr>
<tr><td>Vinyl chloride</td><td>0.32</td><td>PVC</td><td>0.55</td><td>1.71875</td></tr>
<tr><td>Bisphenol A</td><td>0.94</td><td>PC</td><td>1.35</td><td>1.436170213</td></tr>
</table>



Chapter 2

2-1

Mol. Wt. (100 Å) $= (\text{weight/molecule}) \times 6.02 \times 10^{23}$

$= (\pi D^3 \rho/6) \times 6.02 \times 10^{23}$

$= \underline{\underline{3.15 \times 10^5}}$ g/g-mole

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

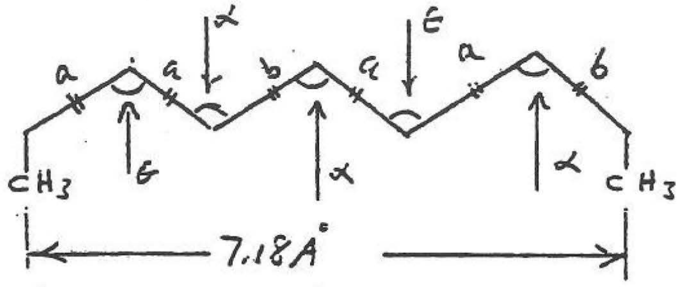
Mol. Wt.(1 cm) = Mol.Wt.(100 Å) $\times 10^{18} = \underline{\underline{3.15 \times 10^{23}}}$ g/g-mole

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 = θ
1.54 " " C-C = b   110° for C-C-O = α

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:

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

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

Same in toluene:

$\chi = 0.557$, $V_1 = 106$, $NV_1 = 2.40 \times 10^{-3}$, 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_o = 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 cm^3

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

2-5 (cont'd):

total weight/cm^3 = 0.931 x 0.80 + 0.069 x 1.2 = 0.745 + 0.083
= 0.828 g/cm^3 (sample density)

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

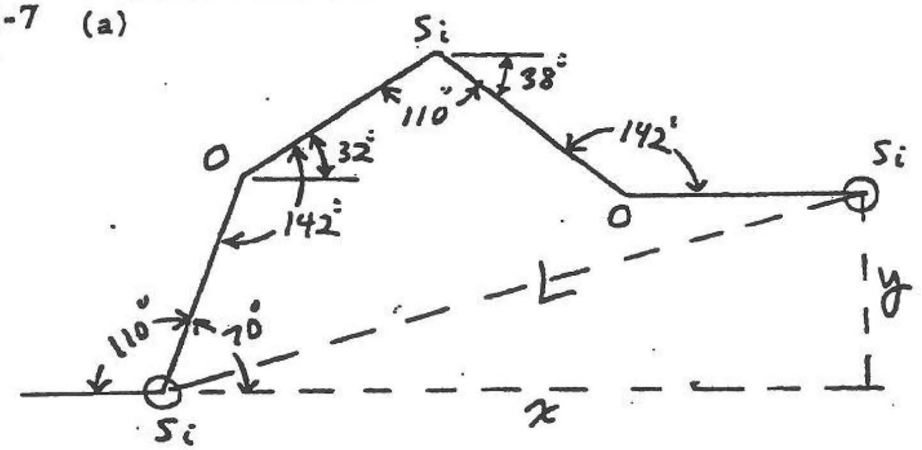
$$Y = 2RV_1X + \chi$$

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

2-7 (a)



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

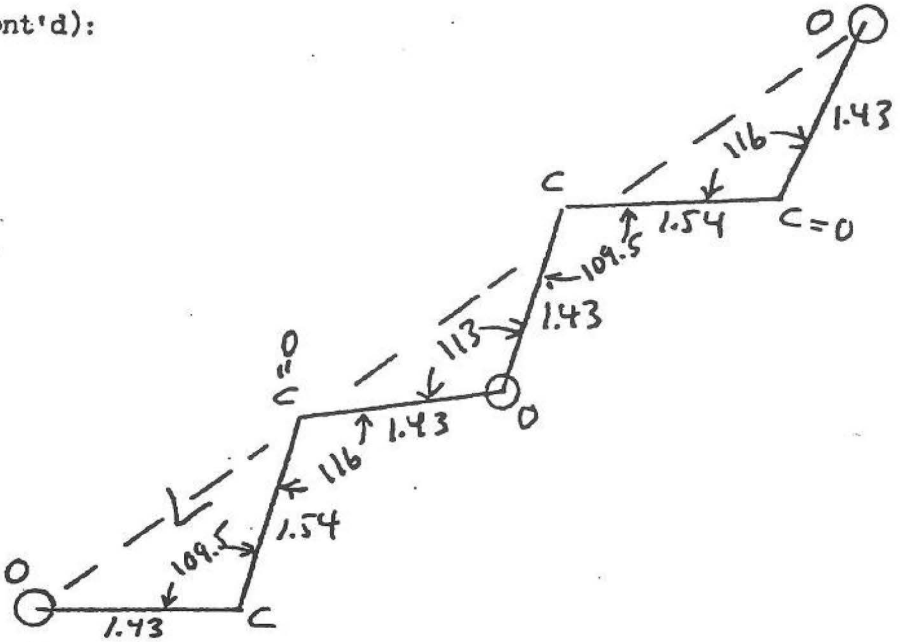
$y = 1.64(\sin 70° + \sin 32° - \sin 38°) = 1.64 \times 0.854$

$L = 1.64 \times 3.098 = 5.080$ Å/2 units, so for 1000 units,

$\Sigma L = 2{,}540$ Å or 254 nm.

2-7 (cont'd):

(b)



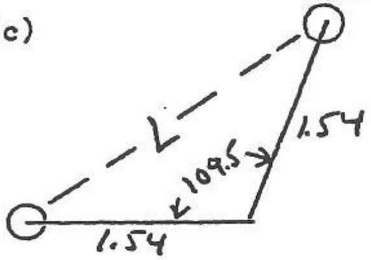
$x = 1.54(\cos 70.5° + \cos 3°) + 1.43(\cos 0° + \cos 6.5° + \cos 73.5° + \cos 67°)$

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

$x = 5.87$, $y = 4.38$, $L = 7.32/2$ units

For 1000 units, ΣL = 366 nm

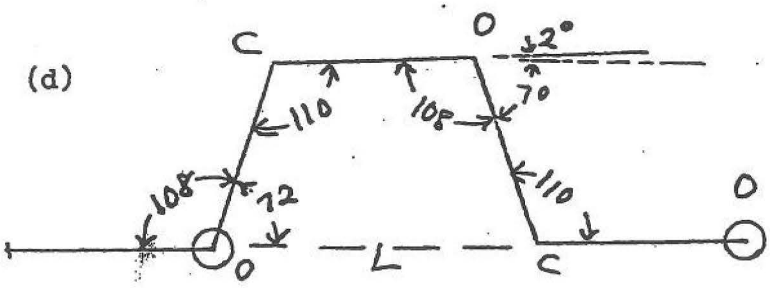
(c)



$L = 2 \times 1.54 \times \cos 35.25° = 2.52$ Å

For 1000 units, ΣL = 252 nm

(d)

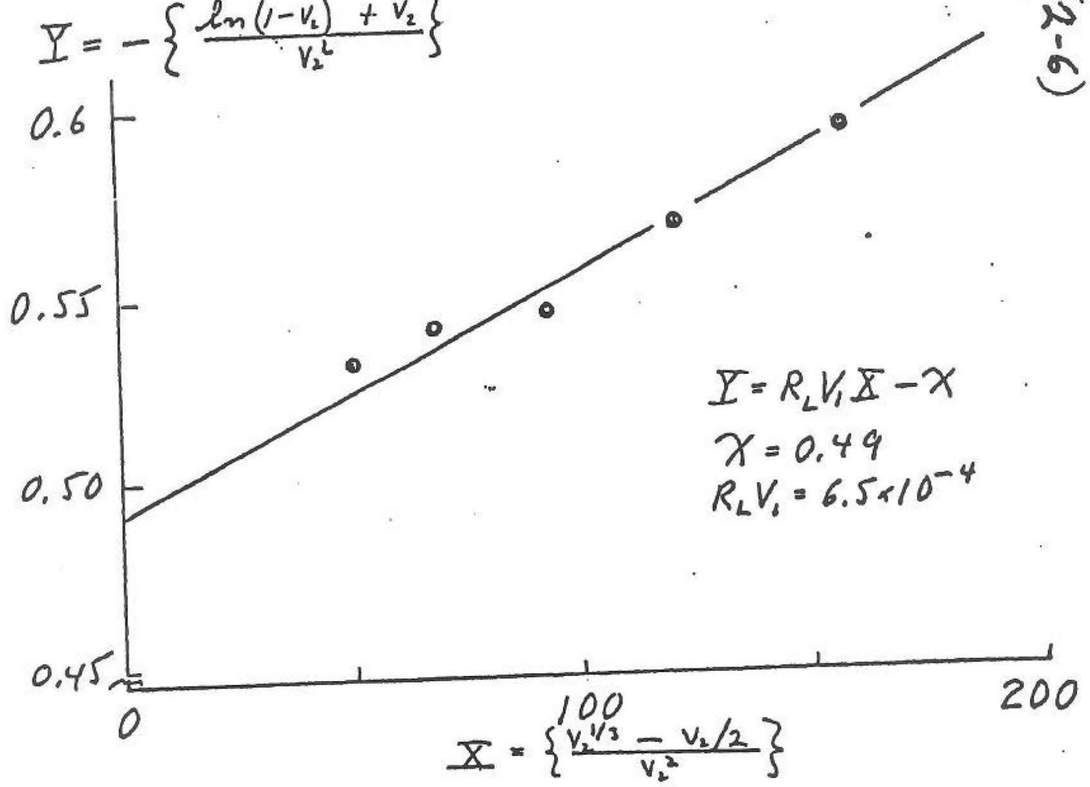


$x = 1.43(\cos 72° + \cos 2° + \cos 70° + \cos 0°) = 3.790$ Å

$y = 1.43(\sin 72° + \sin 2° - \sin 70°) = 0.066$ Å

$L = 3.79$ Å/2 units, For 1000 units, ΣL = 189.5 nm

(2-6)


$\mathrm{Y} = -\left\{ \frac{\ln(1-v_2) + v_2}{v_2^2} \right\}$
0.6
0.55
0.50
0.45
0
100
200
$\mathrm{X} = \left\{ \frac{v_2^{1/3} - v_2/2}{v_2^2} \right\}$
$\mathrm{Y} = R_L V_1 \mathrm{X} - \chi$
$\chi = 0.49$
$R_L V_1 = 6.5 \times 10^{-4}$

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)

$$\text{Volume} = \frac{2 \times 10^{6}\ \text{g}}{6.023 \times 10^{23}\text{molecule}} \frac{1\ \text{cm}^{3}}{\times\ 0.906\ \text{g}} = 0.37 \times 10^{-17}\ \text{cm}^{3}$$

$$'' \quad = \underline{3.7 \times 10^{3}\ \text{nm}^{3}} = 3.7 \times 10^{6}\ \text{Å}^{3}$$

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

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

$v_2 = 1/4.35 = 0.23$

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

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

[Nomograph gives $\chi = 0.41$]

New value of $v_2 = 1/3.45 = 0.29$

Using $\chi = 0.39$ gives $NV_1 = 0.0039$

Using $\chi = 0.41$ gives $NV_1 = 0.0037$

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

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

Therefore, each crosslink contains an equal amount of sulfuir

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

2-10

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

$v_2 = 5/75 = 0.067$

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

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

Case II: Concentration = c_2

We want $v_2 = 5/25 = 0.200$

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

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

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

Thus we need 0.020 x 14.6 = <u>0.29 g of A/100 g P = c_2</u>

2-11

In solvent A:

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

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

From Fig. 2-4, if $\chi_A = 0.33$ at $v_2 = 0.1$, then at $v_2 = 0.2$, χ_B must equal 0.52. That is, $(NV_1) = 5.0 \times 10^{-3}$ in either solvent. Then $\chi_B = \beta_1 + (V_1/RT)(\delta_B - \delta_p)^2$

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

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

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

2-12

N = 2C where C = number of moles of crosslinks

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

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

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

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

Swollen volume = $1/v_2$ = <u>9.5 cm^3</u>

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

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

From Figure 2-4, $v_2 = 0.175$. Swollen volume = $1/v_2$ = 5.71 cm^3

2-14

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

In Q: $\delta_Q = (29{,}900 \times 0.860/88.0)^{1/2} = 17.1$ $(MPa)^{1/2}$

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

New value of (NV_1) in Q = (NV_1) in S x $\{V_1(Q)/V_1S)\} = 8.63 \times 10^{-3} \times (88.0/0.86)/216)$

So f (NV_1) in Q = 4.09×10^{-3} 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

$\chi = 0.300 + [100/(2x300)][7.00 - \delta_p]^2 = 0.300 + [100/(2x300)][8.80 - \delta_p]^2$

So $\pm(7.00 - \delta_p) = 8.80 - \delta_p$

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

$\chi_A = \chi_B = 0.435$ In A: $v_2 = 0.25$

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

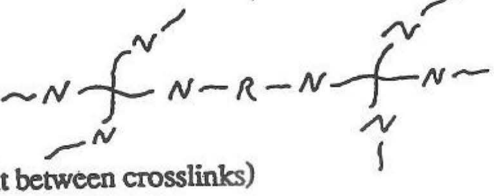
In C: $(NV_1)_C = 2.5\,(NV_1)_A = 5.2 \times 10^{-2}$

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

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

2-16

$\chi = 0.43$, $V_1 = 112.5/1.10 = 102$ cm^3/mol



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

Concentration of chains = 0.5 x concentration of nitrogen

Conc. of nitrogen = (2.10 g/liter)/(14.0 g/ mol of nitrogen) = 0.15 mol/liter

Conc. of chains = 0.15/2 = 0.075 mol/liter

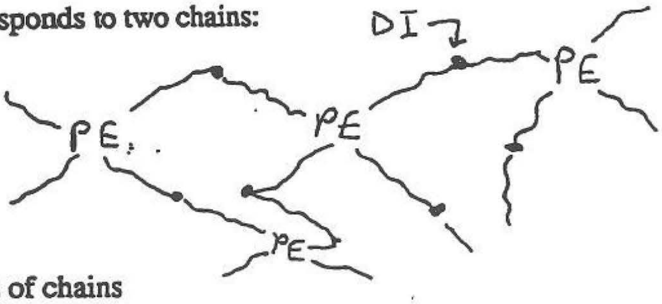
NV_1 = (0.075 mol/liter)x(102 cm^3/mol)x(liter/1000 cm^3) = 7.65×10^{-3}

From equation or nomograph, $v_2 = 0.167 = 1/6.00$

So 1 cm^3 swells to 6.00 cm^3.

2-17

Each PE is a crosslink and corresponds to two chains:



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

$1 \times 136 = 136$

$2 \times 110 = 220$

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

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

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

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

χ (from nomograph or equation) $= 0.50$ (actually 0.495 from equation)

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

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

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

$\delta_2 = \underline{\underline{8.90 \pm 1.04}}$ (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)

Covalent crosslinks/Total crosslinks = 2.13/6.11 = 0.349

Therefore, ester bonds were 1.000 - 0.349 = 0.651 of original total.

2-19

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

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

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

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

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

where V_p is the volume of dry polymer.

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

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:

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

$$= RT\left[-\chi v_1 v_2 + \chi v_2 + \ln(1 - v_2) + v_2 + \varsigma\frac{V_1 v_2^{1/3}}{V_p}\right]$$

$$= RT\left[\chi v_2^2 + \ln(1 - v_2) + v_2 + N V_1 v_2^{1/3}\right]$$

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

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

2-20

a)

$$\Omega_M = \frac{1}{n_2!}\prod_{n_2'=0}^{n_2-1}\frac{(z-1)^{x-1}}{n^{x-1}}(n-xn_2')^x$$

$$\Omega_M = \frac{1}{n_2!}\frac{(z-1)^{n_2(x-1)}}{n^{n_2(x-1)}}\prod_{n_2'=0}^{n_2-1}(n-xn_2')^x$$

$$\Omega_M = \frac{x^{xn_2}}{n_2!}\left(\frac{z-1}{n}\right)^{n_2(x-1)}\prod_{n_2'=0}^{n_2-1}(\frac{n}{x}-n_2')^x \qquad (1)$$

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

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

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

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:

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