

HW#4 Solution Set  
Winter 2001, ChE160/260

#5.1

In a pure polymer in the bulk, mers interact only with other mers, on their own or adjacent chains. These interactions can be considered ideal: there is no change in volume associated with mixing the chains ( $\Delta V_{\text{mix}}=0$ )\* and there is no mixing enthalpy ( $\Delta H_{\text{mix}} = 0$ ). When a polymer chain is present in a solvent, there is in general a swelling or contraction of the polymer which occurs; this can be viewed macroscopically as many types of rubber swell in the presence of organic solvents. Alternately, some polymers will precipitate out of solution when placed in a solvent. In either case there is a change in the radius of gyration compared to the bulk. The theta solvent represents the situation where there is no swelling or contraction compared to the bulk; it is the worst solvent for a polymer which does not cause precipitation.

In a theta solvent the increase in volume (excluded volume) associated with interpenetration of the solvent between the chains and solvent/mer interaction, is exactly balanced by the positive enthalpy of mixing  $\Delta H_{\text{mix}} > 0$ . Perhaps a better way to think of the problem is to consider the forces on a polymer sphere. The solvating effect exerts an osmotic pressure which tends to swell the polymer. The enthalpy of mixing can likewise be related to a pressure, by considering the equation of state  $\Delta H = T\Delta S + V\Delta P + \sum \mu_i \Delta n_i$ . Although  $\Delta S$  is also positive,  $\Delta H > T\Delta S$  in the theta solvent. The last term is zero because the stoichiometry is fixed. Therefore the positive enthalpy of mixing leads to a positive pressure on the sphere. For the theta solvent these two “pressures” on the polymer “sphere” balance so there is no change in the radius of gyration relative to the bulk.

Alternately we can consider the relationship between  $\Delta H_{\text{mix}}$  and pressure from equations 3.25 and 3.21 in Sperling.

\* Actually remember that we considered an excluded volume associated with the inability of a chain to interpenetrate with itself during its random walk in the bulk; this led to the fact that the actual radius of gyration was slightly larger than that given by a random walk process [eqn 5.14 vs. eqn 5.12]. But here we are considering excluded volume due to mixing only.

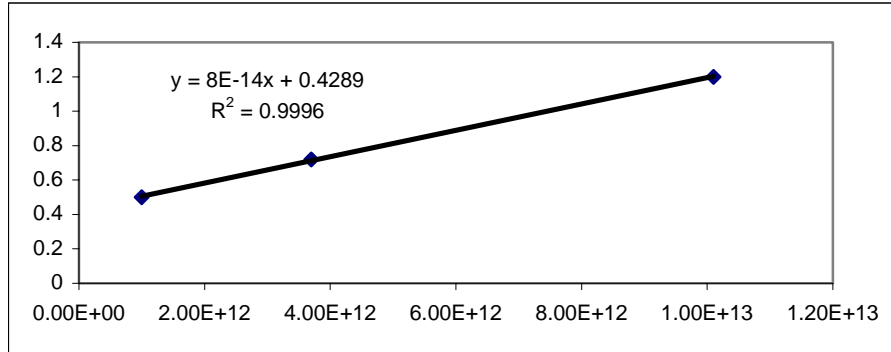
#5.2

There are several ways to estimate the radius of gyration and end-to-end distance. Two such examples are given here. If you note that the ratio  $R_g^2/M_w$  is roughly constant for a given polymer, then from Table 5.4 for polystyrene  $(R_g^2/M_w)^{1/2} = 0.275 \text{ A (mol/g)}^{1/2}$ . For the given polymer this means  $R_g = [ [0.275 \text{ A (mol/g)}^{1/2}]^2 * 1E^5 \text{ g/mol} ]^{1/2} = \mathbf{87 \text{ A}}$ . Then from equation 3.58,  $r_o = R_g\sqrt{6} = \mathbf{213 \text{ A}}$ .

Alternately we can use eqn 5.14 in conjunction with Table 5.7. Then  $C = 9.85$ , 1 carbon-carbon bond distance = 1.54 A from lecture #2, and x is in this case the degree of polymerization. The molecular weight for styrene is 104 g/mol, so  $n = 10^5/104 \sim 962$ . So  $r_f = (9.85 * 1.54^2 * 962)^{1/2} \text{ A} = 149.9 \text{ A} \sim \mathbf{150 \text{ A}}$ . Then  $R_g = r_f/\sqrt{6} = \mathbf{61.2 \text{ A}}$ .

#5.6

This is a fairly straightforward problem. From equation 5.11, neglecting higher order terms, if  $(d\Omega/d\Sigma)^{-1}$  is plotted versus  $K^2$ , then the intercept is given by  $(C_n M_w)^{-1}$  and the slope is given by  $R_g^2/3 * (C_n M_w)^{-1}$ . This plot is shown below:



So  $M_w = (1/0.4289 \text{ cm}) * (1/10E^{-5} \text{ mol/g cm}) = \mathbf{23315 \text{ g/mol}}$

And  $R_g^2 = 3 * 10E^{-5} \text{ mol/g cm} * 23315 \text{ g/mol} * 8E^{-14} \text{ cm}^3 = 5.36 E^{-17} \text{ cm}^2 = 5355.6 \text{ \AA}^2$

So  $R_g = \mathbf{73.2 \text{ \AA}}$

Implicit in the equation utilized is the fact that the second virial coefficient,  $A_2 = 0$ . This is probably true for the given situation in that we are distributing a tagged polymer which is structurally the same as the host matrix except that it is deuterated. This should not effect the mixing too much and thus the system behaves as a pure bulk polymer with  $A_2 = 0$ .

#5.7

The data in table 5.10 shows two diffusion coefficients for 3-star polymers of the same molecular weight at two different temperatures. Assuming an Arrhenius behavior, then  $D = D_0 \exp(-E/RT)$ . We are asked to solve for E. Taking the ratio of this equation at two different temperatures cancels  $D_0$ . Taking the natural log of both sides and rearranging yields:

$$k * (1/T_2 - 1/T_1)^{-1} * \ln(D_1/D_2) = E.$$

$$8.314 \text{ J/molK} * (1/(165+273) - 1/(125+273))^{-1} * \ln(2.4E-14/1.4E-13) = E$$

$$\mathbf{E = 63900 \text{ J/mol} = 63.9 \text{ kJ/mol}}$$

To interpret this result takes some creativity. We can compare it to the thermal energy at room temperature for example =  $RT = 2.45 \text{ kJ/mol}$  and find that it is ~ 26 times larger. So diffusion is only appreciable at temperatures much higher than room temperature. We can assume that the preexponential factors are the same for the linear and star shaped polybutadienes and compare activation energies. We will use the cases where  $T_1 = T_2 = T = 125^\circ\text{C}$ , so

$$E_2 = E_1 + RT \ln(D_1/D_2) = 63.9 \text{ kJ/mol} + 8.314E^{-3} \text{ kJ/mol K} * 398^\circ\text{K} * \ln(2.4E^{-14}/4.8E^{-11})$$

$$E_2 = 38.1 \text{ kJ/mol}$$

Thus the activation energy for the linear polymer is much lower than that for the star polymer. We can interpret this result now by considering how the star polymer would have to diffuse in a concentrated (bulk) sample. To move in a reptative fashion, one of the arms of the polymer will need to collapse in line so that the polymer is linear. This substantially reduces the configurational entropy of the polymer resulting in the high activation energy. Note that the activation energy for the linear polymer is still much larger than the thermal energy at room temperature.

## #6.2

This was, unfortunately, a very confusing problem if you tried to consider the exact models extolled in the reading. Since the problem called for an estimate, however we make the following assumptions.

- 1) The growth rates given in Table 6.6 are applicable and give G in units of cm/s for T in K and R in J/molK.
- 2) The instantaneous nuclei density is fixed with respect to temperature/undercooling.
- 3) Nuclei grow as spheres isotropically.
- 4) The melting point of the polyethylene is 145°C.

Obviously assumptions two and three run completely counter to the models for which the growth rates were derived, but without further information on the geometry of the lamellae we cannot stick with the model.

With assumptions 2/3, we can estimate the linear distance between nucleation sites to be  $L = 1/\sqrt[3]{10^4 \text{ cm}^3} = 0.046416 \text{ cm}$ . Once a total growth of  $0.046416/2 = 0.023208 \text{ cm}$  has occurred we assume nucleation is complete. We divide by two as nucleation occurs from both adjacent nuclei. We have reduced the three dimensional problem of growing spheres to a one dimensional problem of growing lines. Note that  $n_z = 30,000 \text{ g/mol} \div 14 \text{ g/mol} = 2142.9$ .

We write the temperature as a function of time  $T = (145+273 \text{ }^\circ\text{K}) - CR/60 t$ , with time t in seconds, and CR=cooling rate in  $^\circ\text{K}/\text{min}$ . Then  $\Delta T = 418-T = CR/60 t$ . For each of the growth rates we calculate the length of growth attained in regimes I and II, by substituting T and  $\Delta T$  into the growth rate equations and integrating over the appropriate time integral. These intervals are...

CR ( $^\circ\text{C}/\text{min}$ )	Time spent in Region I (s)	Time spent in Region II (s)
1	0 – 960	960 – 1072
100	0 - 9.6	9.6 – 13.8

The results, done with Maple (see pages at the end of this document) are summarized below:

Cooling Rate	Growth in I (cm)	Growth in II (cm)	% in I	% in II
1 °C/min	0.06738	0.40137	<b>100</b>	<b>0</b>
100 °C/min	0.0006738	0.113889	<b>2.9</b>	<b>97.1</b>

The % in each region is calculated by taking the growth in that region and dividing by 0.023208 cm, as long as the number in that column plus that in the previous column does not surpass 0.023208 cm. If the latter happens, then we know growth finished in the regime in question and the % in that regime is 100% - the entry in the previous column. With both of the growth rates, crystallization is done before the third regime is reached. With the slower cooling rate it occurs completely in Regime I. With the faster cooling rate it occurs predominantly in regime II.

#### #6.8

The theoretical density for a 100% crystalline polymer can be calculated considering a single unit cell, since this completely represents the sample via many replications and translations of the unit cell. The hint suggests using Table 6.2 which gives the answer in the furthest column. However it gives the really pertinent information in the second column. It tells us that the stable form has dimensions a,b,c given and is orthorhombic. Orthorhombic means that the unit cell is a rectangular prism (the three angles between coordinate axes are all ninety degrees) but  $a \neq b \neq c$ . The volume of the unit cell is just abc since it is a rectangular prism.

By considering figure 6.5, we note that there are two  $C_2H_4$  units per cell. The rationale is as follows. The unit cell is body-centered, so one chain is completely within the unit cell. The other four chains shown are each shared by four adjacent unit cells, thus they each contribute only  $\frac{1}{4}$  of a repeat unit ( $C_2H_4$ ); but there are four of them,  $4 * \frac{1}{4} = 1$ . So the total mass per unit cell in amu is  $4 * 12 + 8 = 56$  amu.

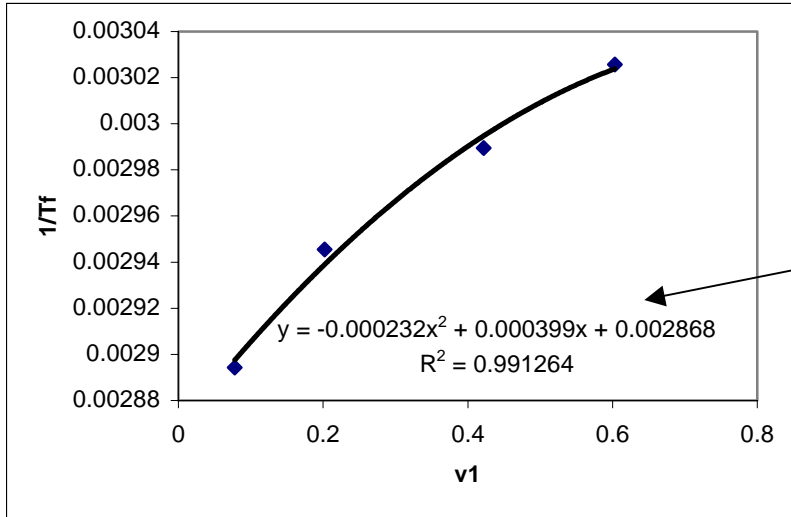
$$\rho = 1 / ( 7.147 * 4.945 * 2.547 \text{ \AA}^3 ) 10^{24} (\text{\AA}^3/\text{cm}^3) * 56 \text{ g}/(\text{mol Unit Cell}) \div 6.023 \text{ E}^{-23} (\text{unit cells})/(\text{mol unit cell})$$

$$\rho = \mathbf{1.033 \text{ g/cm}^3}$$

This agrees quite well with the value of  $1 \text{ g/cm}^3$  given in the table.

#6.10

We can fit the data to equation 6.43, which contains all the quantities asked for in parts a and b. If we plot  $1/T_f$  vs.  $v_1$ , and fit with a second order polynomial, the coefficient to  $v_1^0 = 1/T_f^0$ , the melting point of the pure polymer, the coefficient to  $v_1$  is  $RV_u/(\Delta H_f V_1)$ , and the coefficient to  $v_1^2$  is  $-RV_u/(\Delta H_f V_1)\chi_1$ . The results of such a fit with Excel are shown below.



Note that you really need to have several digits here to get accurate values... Using 0.002 vs. 0.002686 gives a difference of almost 5°.

So we find that

$$T_f^0 = 1/0.002868 = 348.7^\circ \text{ K} = \mathbf{75.7^\circ \text{ C}}$$

$$RV_u/(\Delta H_f V_1) = 0.000399 \text{ K}^{-1}$$

Calculate from picture I emailed out.

$$V_u = \text{molar volume of mer} = 284 \text{ g/mol} / (0.99 \text{ g/cm}^3) = 286.87 \text{ cm}^3/\text{mol}$$

$$V_1 = \text{molar volume of solvent} = 73 \text{ g/mol} / (0.9445 \text{ g/cm}^3) = 77.29 \text{ cm}^3/\text{mol}$$

$$\Delta H_f = RV_u/0.000399V_1 = 8.314 \text{ J/molK} * (286.67/77.29) \div 0.000399\text{K}^{-1} = 77285.2 \text{ J/mol} = \mathbf{77.3 \text{ kJ/mol}}$$

$$-RV_u/(\Delta H_f V_1)\chi_1 = -0.000232 \text{ K}^{-1}$$

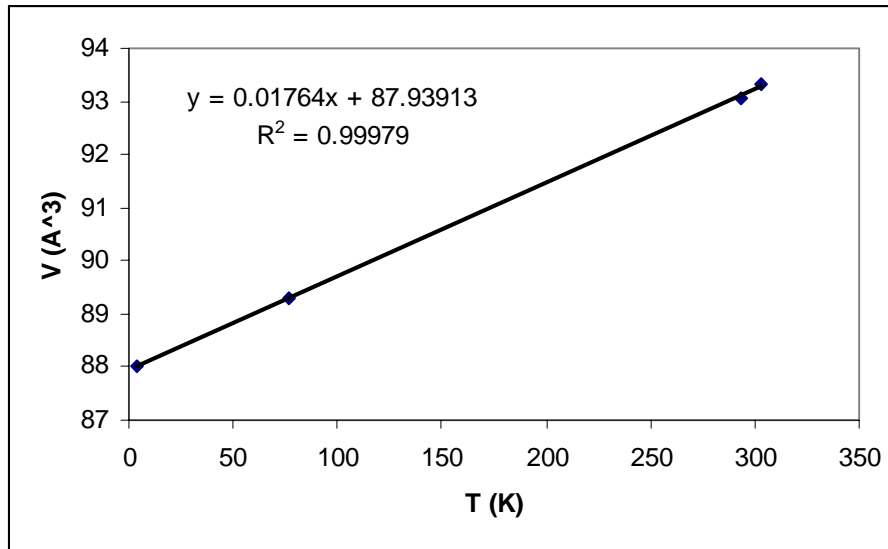
$$\chi_1 = 0.000232 \text{ K}^{-1} RV_u/(\Delta H_f V_1) = 0.000232/0.000399$$

$$\chi_1 = \mathbf{0.58}$$

Note that since  $\chi_1$  is positive, the mixing process between the solvent and polymer is endothermic,  $\Delta H_f$ . The paper from which this problem was obtained is included in a handout made for one of the Tuesday night review sessions.

#6.16

a) Again this data is for polyethylene, so as in problem 6.8 the volume of the unit cell is given by the product  $abc$ . A linear plot of volume vs. temperature gives a slope of  $0.01764 \text{ \AA}^3/\text{K}$ .



Using the average volume over this entire temperature range then gives

$$\alpha = 1/90.9255 \text{ \AA}^3 (0.01764 \text{ \AA}^3/\text{K}) = \mathbf{1.94 \text{ E}^{-4} \text{ K}^{-1}}$$

Note that if we were interested in a particular temperature range, we would be better suited to use the value of volume in that regime obtained from the equation in the graph. For example if we wanted  $\alpha$  at  $200^\circ\text{K}$ , we should use a value of  $V = 91.47 \text{ \AA}^3$ . Then

$$\alpha = 1.929 \text{ E}^{-3} \text{ K}^{-1}.$$

b) The C-C bonds of the polymer run along the c-axis of the unit cell. Since these covalent bonds are quite stiff compared to the energy required to separate chains (related to soft hydrogen bonding/Van der Waals forces) volume expansion is accommodated by chain separation rather than interatomic bond stretching.

Maple Results, question 6.2, Cooling Rate 1°C/min

> **T:=(145+273) - CR/60\*t;**

$$T := 418 - \frac{1}{60} CR t$$

> **dT:=CR/60\*t;**

$$dT := \frac{1}{60} CR t$$

> **CR:=1;**

$$CR := 1$$

> **nz:=2142.9;**

$$nz := 2142.9$$

> **R:=8.314;**

$$R := 8.314$$

> **GI:=5E13/nz\*exp(-7000/(R\*T)-1.8E5/(T\*dT));**

$$GI := .2333286668 \cdot 10^{11} e^{\left(-841.9533318 \frac{1}{418 - 1/60 t} - \frac{.1080 \cdot 10^8}{(418 - 1/60 t) t}\right)}$$

> **GII:=3.34E7/nz\*exp(-7000/(R\*T)-0.9E5/(T\*dT));**

$$GII := 15586.35494 e^{\left(-841.9533318 \frac{1}{418 - 1/60 t} - \frac{.540 \cdot 10^7}{(418 - 1/60 t) t}\right)}$$

> **evalf(int(GI, t=0..960));**

$$.06738085640$$

>

> **evalf(int(GII, t=960..1072));**

$$.4013739105$$

>

Maple Results, question 6.2, Cooling Rate 100°C/min

> **T:=(145+273) - CR/60\*t;**

$$T := 418 - \frac{1}{60} CR t$$

> **dT:=CR/60\*t;**

$$dT := \frac{1}{60} CR t$$

> **CR:=100;**

$$CR := 100$$

> **nz:=2142.9;**

$$nz := 2142.9$$

> **R:=8.314;**

$$R := 8.314$$

> **GI:=5E13/nz\*exp(-7000/(R\*T)-1.8E5/(T\*dT));**

$$GI := .2333286668 \cdot 10^{11} e^{\left(-841.9533318 \frac{1}{418 - 5/3 t} - \frac{108000.0000}{(418 - 5/3 t) t}\right)}$$

> **GII:=3.34E7/nz\*exp(-7000/(R\*T)-0.9E5/(T\*dT));**

$$GII := 15586.35494 e^{\left(-841.9533318 \frac{1}{418 - 5/3 t} - \frac{54000.00000}{(418 - 5/3 t) t}\right)}$$

> **evalf(int(GI, t=0..9.6));**

$$.0006738084992$$

>

> **evalf(int(GII, t=9.6..13.8));**

$$.1138885699$$

>