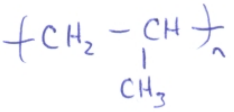
Problem Set #1 Solutions
Chemical Engineering 160/260

Chapter #1

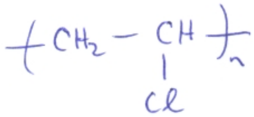
#2. polyethylene $\left(CH_2 - CH_2 \right)_n$

polypropylene



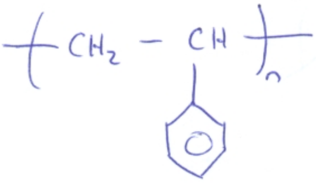
$$\left(CH_2 - \underset{\substack{|\\ CH_3}}{CH} \right)_n$$

poly(vinyl chloride)



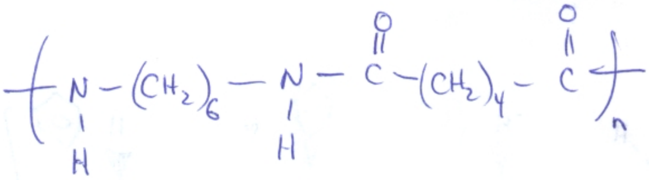
$$\left(CH_2 - \underset{\substack{|\\ Cl}}{CH} \right)_n$$

polystyrene



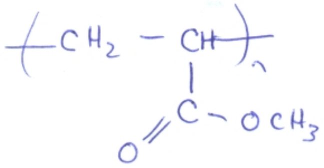
formulas assume head to tail addition.

Nylon 6,6



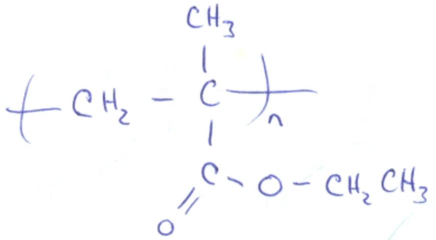
$$\left(\underset{\substack{|\\ H}}{N} - (CH_2)_6 - \underset{\substack{|\\ H}}{N} - \overset{\substack{O\\ \|}}{C} - (CH_2)_4 - \overset{\substack{O\\ \|}}{C} \right)_n$$

#3. a)



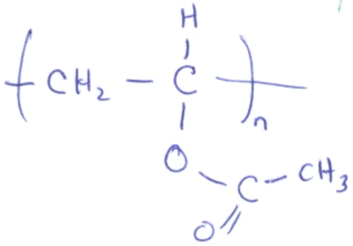
poly(methyl acrylate)

b)



poly(ethyl methacrylate)

c)



poly(vinyl acetate)

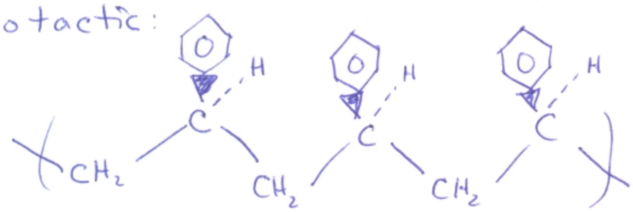
d) $\left(CH_2 - CF_2 \right)_n$ poly(1,1-difluoroethylene)

or

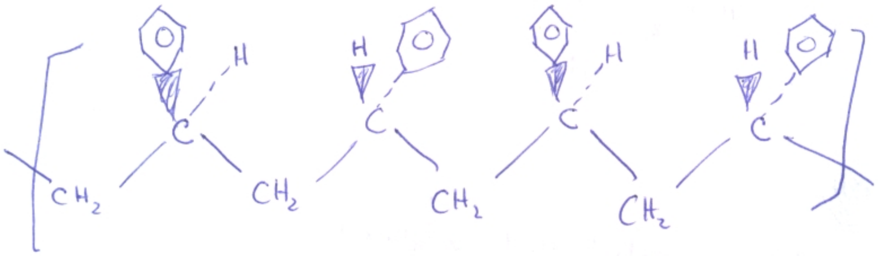
poly(vinylidene fluoride)

Chapter #2

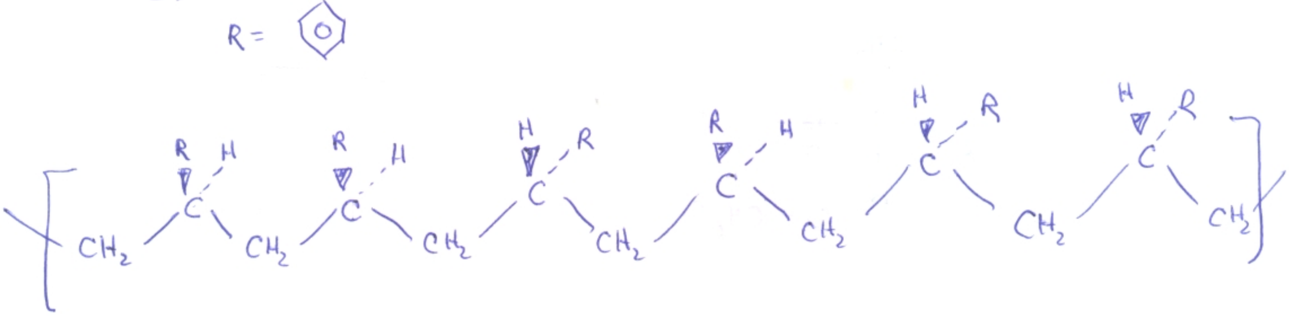
1) isotactic:



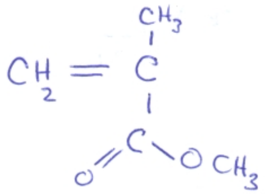
syndiotactic:



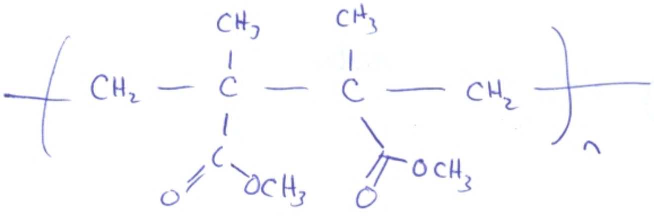
atactic (eg)



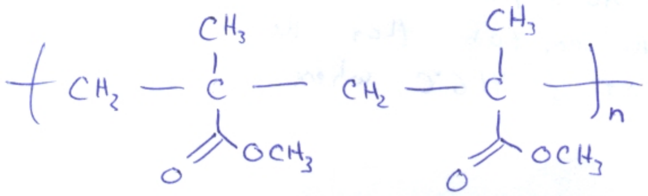
#3 mer :



Head to Head :



Head to Tail :



➡ Renember head to tail addition is more common due to stearic hindrances

Chapter 3

#8. One approach which is a slight approximation but should be valid within experimental error is due use the data in figure 3.7 for $T = 41°C$, and assume $A_2 = 0$. Actually $A_2 = 0$ at $T = 41.6°C$ in DMF for cellulose tricaproate.

$$\frac{\pi}{c} = RT\left(\frac{1}{M_n} + \overset{0}{\cancel{H.O.T.s}}\right) \Rightarrow M_n = RT\left(\frac{c}{\pi}\right)$$

From the figure $10^4 \frac{\pi}{c} \sim 2 \frac{atm L}{g}$

$$\frac{\pi}{c} = 2E^{-4} \frac{atm L}{g}$$

$$M_n = \left(0.08205 \ \frac{\text{atm L}}{\text{mol }^\circ\text{K}}\right)\left(41.6 + 273 \ ^\circ\text{K}\right)\left(\frac{1 \quad \text{g}}{2E^{-4} \ \text{atm L}}\right)$$

$$\boxed{M_n = 129,100 \ \text{g/mol}}$$

#10. Figure 3.14 shows a Zimm plot. We can solve for R_g and M_w using the curves $c=0$ and $\theta=0$ in conjunction with equations 3. and 3.

Other curves ($c \neq 0$ or $\theta \neq 0$) are also usable.

Eqn
$$\left[H \frac{c}{R(\theta)}\right]_{\theta=0} = \frac{1}{M_w} + 2A_2 c$$

But the line $\theta=0$ has no slope, so $A_2=0$. we are also told in the caption that the plot was done in DMF at 41.6°C where DMF is a θ-solvent.

$$M_w = \frac{1}{\left[H \frac{c}{R(\theta)}\right]_{\theta=0}} = \frac{1}{6.05E^{-7} \ \text{mol/g}}$$

$$\boxed{M_w \sim 1.65 \ E^6 \ \text{g/mol}}$$

Eqn
$$\left[H \frac{c}{R(\theta)}\right]_{c=0} = \frac{1}{M_w}\left[1 + \frac{1}{3}\left(\frac{4\pi}{\lambda'}\right)^2 R_g^2 \sin^2\frac{\theta}{2}\right]$$

$$\lambda' = \frac{\lambda}{n_o} = \text{wavelength in solution}$$

Solving for R_g^2

$$R_g^2 = \frac{3\left(\frac{\lambda}{4\pi n_o}\right)^2}{\sin^2\left(\frac{\theta}{2}\right)} M_w \left[H \frac{c}{R(\theta)}\right]_{c=0}$$

Plugging in values
$M_w = 1.65E^6$ g/mol
$\lambda = 5461$ Å
$n_o = 1.429$

$$* \quad R_g^2 = 4.586E^{11}\left[\frac{H \frac{c}{R(\theta)}}{\sin^2 \theta/2}\right] - \frac{2.774E^5}{\sin^2\frac{\theta}{2}}$$

There is some difficulty associated with accurately determining values of $\sin^2\theta/2$ and $H\frac{c}{R(\theta)}$ from the graph. Here are values I obtained (yours may differ slightly)

$H\frac{c}{R(\theta)}\left(\frac{mol}{g}\right)$	$\sin^2\left(\frac{\theta}{2}\right)$
$15E^{-7}$	$\frac{2}{29}\cdot 5$
$25E^{-7}$	$\frac{3.5}{29}\cdot 5$

Substituting back into * gives

$$R_g^2 = 1.19E^6\,\text{Å}^2 \Rightarrow R_g = 1091\,\text{Å}$$

$$R_g^2 = 1.44E^6\,\text{Å}^2 \Rightarrow R_g = 1200\,\text{Å}$$

$$\boxed{\therefore R_g \sim 1100\,\text{Å}}$$

#12 This part has two problem: first we calculate $\frac{\bar{r}_0^2}{m}$ from Table 3.11. Then we calculate the corresponding value from Table 3.9.

Part #1

We are told to use equation 3.82. Values for Φ are given in the text. Note that there is a units problem with the reported values, or with the equation.

$$\underset{\overset{\uparrow}{\frac{mL}{g}}}{K} = \underset{\overset{\uparrow}{\frac{mL\,g^{\frac{1}{2}}}{cm^3 mol^{3/2}}}}{\Phi}\underset{\overset{\uparrow}{\left(\frac{cm^2 mol}{g}\right)^{3/2}}}{\left[\frac{\bar{r}_0^{2}}{m}\right]^{3/2}}$$

Actually this is just sorta the nature of the equation. The "units" of Φ should in theory vary with the exponent a. So I don't think Sperling's really made any mistake.

~~I'll assume Sperling has made a mistake in reporting~~
~~the units, but not values of Φ.~~

$$\Phi_1 = 3.6E^{21} \frac{dL\, g^{1/2}}{cm^3\ mol^{3/2}}$$

$$K = 84.6\,E^{-3} \frac{mL}{g}$$ from the table for polystyrene in cyclohexane

$$\Phi_2 = 2.1E^{21} \frac{dL g^{1/2}}{cm^3\ mol^{3/2}}$$

$$\text{w/ } \Phi_1 \rightarrow \left(\frac{\bar{r}_0^2}{m}\right)^{3/2} = \frac{84.6\ E^{-3}}{2.1E^{21}} \frac{mL}{g^{3/2}} \cdot \frac{cm^3\ mol^{3/2}}{dL} \cdot 10^{-2} \frac{dL}{mL}$$

$$\left(\frac{\bar{r}_0^2}{m}\right)^{3/2} = 2.35\ E^{-25}\ cm^3 \left(\frac{mol}{g}\right)^{3/2}$$

$$\boxed{\left(\frac{\bar{r}_0^2}{m}\right)_1 = 3.8081\ E^{-17}\ \frac{mol}{g}\, cm^2}$$

$$\text{w/ } \Phi_2 \rightarrow$$

$$\left(\frac{\bar{r}_0^2}{m}\right)^{3/2} = \frac{84.6\ E^{-3}}{2.1\ E^{21}} \cdot 10^{-2} = 4.0286E^{-25}\ cm^3 \left(\frac{mol}{g}\right)^{3/2}$$

$$\boxed{\left(\frac{\bar{r}_0^2}{m}\right)_2 = 5.4547\ E^{-17}\ \frac{mol}{g}\, cm^2}$$

Part #2

Table 3.9 gives a value of $\langle R_g \rangle^2 = 6.51\ E^{-12} cm^2$ for a polymer of polystyrene in cyclohexane at 34.2 °C with M_w = 7.65 E⁵ g/mol. This temperature is quite close to the Θ-temperature 34.8 °C. ~~we can check We must assume the molecular weight applies~~

Assume that the polymer assumes a random coil configuration in this solution. Then $R_g^2 = r_0^2/6$

$$\therefore \frac{r_0^2}{m} = \frac{6R_g^2}{m} = \frac{6(6.51E^{-12}\ cm^2)\ mol}{7.65\ E5\ g} = 5.1059E^{-17}\ \frac{cm^2\ mol}{g}$$

This agrees fairly well with those calculated previously based on Table 3.11.

#15 Figure 3.18 is a plot of $\log[\eta]$ vs. $\log M_w$ for polystyrene in toluene, benzene and dichloroethylene at 30 °C. We are asked to determine K and a in the Mark-Houwink equation $[\eta] = K M_v^a$.

$$\log[\eta] = \log K + a \log M_v$$

Thus if we determine two points for each solvent we can solve for K and a.

benzene

$\log \eta$	$\log M_w$
0.0625	5.5
0.5	6

$$a = \frac{\Delta \log \eta}{\Delta \log M_v} = \frac{0.5 - 0.0625}{0.5}$$

$$\boxed{a = 0.775}$$

$$\log K = \log \eta - a \log M_w$$

$$\log K = -4.2$$

$10^{-4.2} = 6.31E^{-5}$

$$K = 10^{-4.2}$$

$$\boxed{K = \text{[redacted]}\ 6.31E^{-5}\ \frac{mL}{g}}$$

toluene

$\log \eta$	$\log M_w$
0.45	6
0.8125	6.5

$$a = \frac{0.8125 - 0.45}{0.5}$$

$$\boxed{a = 0.725}$$

$$\log K = 0.45 - (6)(0.725) = -3.9$$

$$\boxed{K = 10^{-3.9} = \text{[redacted]}\ 1.25E^{-4}\ \frac{mL}{g}}$$

dichloroethylene

$\log \eta$	$\log M_w$
-0.025	5.5
0.3625	6

$$a = \frac{0.3625 + 0.025}{0.5}$$

$$\boxed{a = 0.775}$$

$$\log K = 0.3625 - (6)(0.775) = -4.2875$$

$$\boxed{K = \text{[redacted]}\ 5.158E^{-5}\ \frac{mL}{g}}$$

$5.158E^{-5}$

#16. We are asked to determine the relationships between α, R_g and $[\eta]$ from data in a Table, and to explain if α and $[\eta]$ can be theoretically related.

Theory

$\alpha = \frac{R_e}{R_{e_0}}$, where R_e is a hydrodynamic radius describing roughly a polymer's size in solution. By definition it is quite similar to the radius of gyration. So we can assume $R_g \propto R_e$ and $\alpha = \frac{R_g}{R_{g\theta}}$.

This allows us to calculate α, using the value for $\langle R_g^2 \rangle$ at $T = 34.2°C$, where $A_2 \sim 0$ as $\langle R_{g\theta} \rangle^2$. These results are shown below:

$\alpha = \left[\frac{\langle R_g^2 \rangle}{\langle R_{g\theta}^2 \rangle}\right]^{1/2}$	T (°C)
1.173	60.1
1.135	50.1
1.107	45.4
1.078	40.2
1.055	37.3
1.020	35.2
1.000 (reference)	34.2
0.948	32.2

Now we are asked to related α, $[\eta]$ and R_g.

From definition,

$$\boxed{\alpha \sim R_g}$$

where I will use $\sim$ to mean proportional in deference to conflict with the chain expansion variable α.

From analysis of the data in the table, it becomes clear that

$\boxed{[\eta] \sim \langle R_g^2 \rangle}$ The relevant calculations follow:

$\frac{\langle R_g^2 \rangle E^{12}}{[\eta]}$	T (°C)
7.791	60.1
8.067	50.1
8.102	45.4
8.253	40.2
8.45	37.3
8.286	35.2
8.209	34.2
7.810	32.2

Average: 8.121
Standard Deviation: 0.230

Because we derived α from R_g, it follows that

$$\boxed{\alpha^2 \sim [\eta]}$$

T °C	$\alpha^2/[\eta]$
60.1	1.197
50.1	1.239
45.4	1.244
40.2	1.268
37.3	1.298
35.2	1.273
34.2	1.261
32.2	1.2

Average: 1.247
Stand Deviation: 0.035

Note: there are other valid ways to approach this problem. For example α can be obtained from intrinsic viscosity as $\alpha = \frac{[\eta]}{[\eta]_\theta}$, where $[\eta]_\theta$ would be the value at $T = 34.6°C$ (or $34.2°C$ would be fine).

The we would find that

$\alpha \sim \langle R_g^2 \rangle$, since the table shows $[\eta] \sim \langle R_g^2 \rangle$.

⇒ Either way we are led to a discrepancy with theory. Flory theory predicts that

$$\boxed{[\eta] \sim \alpha^3}$$

: the relevant equation listed in the text is

$$[\eta] = 2.5\, \frac{4\pi}{3} N \left(\frac{R_{E0}}{m}\right)^2 m^{1/2} \alpha^3$$

Avogadro's number

Constant for given polymer

(which incidentally answers the second half of the question.)

which conflicts with the result

$[\eta] \sim \alpha^2$ obtained when α is calculated from R_g values.

Alternately if α is derived from $[\eta]$, then we get

$\alpha \sim \langle R_g^2 \rangle$ in contradiction to its definition

$\alpha \sim \langle R_g^2 \rangle$ ← quadratic

$\alpha = \frac{R_E}{R_{E0}}$ ← linear

The exact cause of the discrepancy is not clear from the data we have. It is possible that Flory's theory relating $[\eta]$ to α^3 does not apply in this particular case, or that the hypothesis $R_E \sim R_g$ is invalid.

#20. $[\eta] = 5.5\ cm^3/g$

$V = 160\ cm^3 = 32$ in $\frac{V\ cm^3}{5}$ units.

From the universal calibration curve in the text, this corresponds to $[\eta]\hat{m}_r$ slightly higher than 10^5. For more precision we need to use a ruler and relate the linear extrapolation between 10^5 and 10^8 to the appropriate value on the log plot. I get ~~10^4~~. $10^{5.125}$

$$\therefore\ 10^{5.125} = [\eta]\hat{m}_r$$

assume this has standard units $\frac{cm^3}{g} \cdot \frac{g}{mol} = \frac{cm^3}{mol}$

$$\hat{m}_r = \frac{10^{5.125}\ \frac{cm^3}{mol}}{5.5\ cm^3/g}$$

$$\boxed{\hat{m}_r = 24{,}250\ g/mol}$$