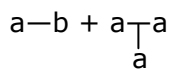


**Lecture 8: Network Formation, Statistical Approach, Pw Based, A Word on MWD for Nonlinear Polymerization**

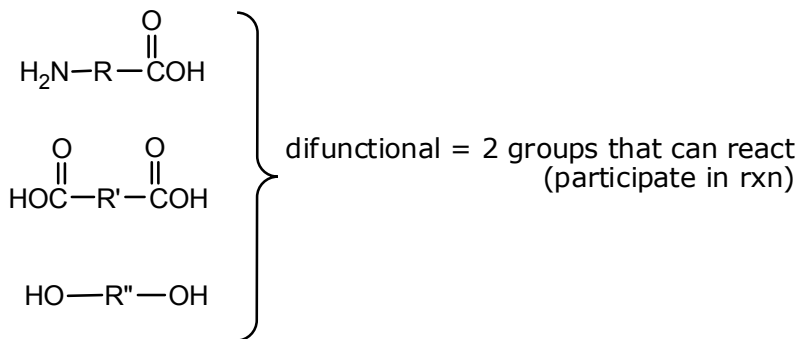
**Network formation**

Consider first case:

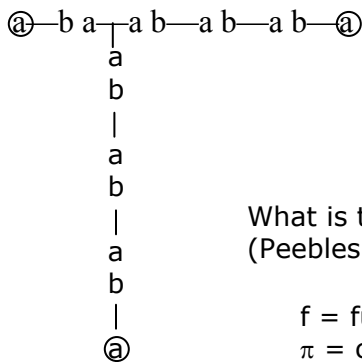
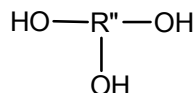


[a<sub>3</sub>]

monomers so far have been difunctional



trifunctional:



Always end in 'a' group  
 Forms branches, not crosslinks

What is the molecular weight or MW distribution?  
 (Peebles, Schaeffgen, Flory) for a-b + a<sub>f</sub> systems

f = func of a<sub>f</sub>  
 π = conversion of b-groups (b=minority)

$$r = \frac{(N_B)_o}{(N_A)_o} \leq 1.0$$

$$\bar{p}_n = \frac{fr\pi + 1 - r\pi}{1 - r\pi}$$

$$\bar{p}_w = \frac{(f-1)^2(r\pi)^2 + (3f-2)r\pi + 1}{(fr\pi + 1 - r\pi)(1 - r\pi)}$$

$$\frac{\overline{p_w}}{p_n} = z = \frac{1 + fr\pi}{(fr\pi + 1 - r\pi)^2}$$

polydispersity

Consider limit as  $r \rightarrow 1.0$

$$\lim_{r \rightarrow 1.0} z = \frac{\overline{p_w}}{p_n} = 1 + \frac{1}{f} \quad \begin{matrix} (r \rightarrow 1.0) \\ (\pi = 1.0) \end{matrix}$$

Specific cases:

Let  $f = 1 \Rightarrow a-b + \underbrace{a-x}$   
end capper

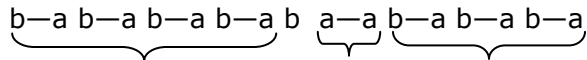
same as  $a-b + \text{end capper}$

$\Rightarrow z = 2.0 \Rightarrow$  same result discussed for general difunctional systems

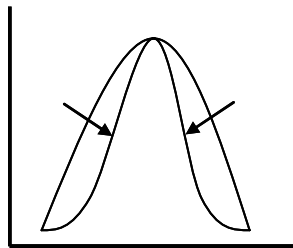
let  $f = 2 \rightarrow a-b + a-a$   
linear polymer

$z = 1 + \frac{1}{2} = 1.5 \rightarrow$  narrower MWD  
does this make sense?

Recall:  $a-b + a-a :$



Join 2 chains together with  $a-a$   
Get rid of extremities of MWD.  
Longer chains are joined together with short chain.  
Long chains can join w/long chains but much less likely.



Consider an example with  $a_f$ :

1 mol  $a-b + 10^{-2}$  mol  $a_3$ :  
(0.01)

$f = 3$

1 b group to 1.03 a groups

Note: for  $r = 0.97$  and  
typical  $a-b$  polymerization:

$$\overline{p_n} = 66 = \frac{1+r}{1-r}$$

$$r = \frac{1}{1.03} \cong 0.97$$

$$\bar{p}_n = \frac{3(0.97) - 0.97 + 1}{1 - 0.97} \cong 99$$

## Systems forming networks

Soluble fraction → "sol"

Polymer chains, oligomers, monomers not connected to network

Gel fraction → insoluble, intractable

⇒ constitutes network

Gel point:  $\pi$  at which an infinite network is formed ⇒  $\pi_c$

Above gel point  $\pi_c$ : gel fraction ↑  
sol fraction ↓

Determine  $\pi_c$  as:  $\bar{p}_n \rightarrow \infty$   
 $\bar{p}_w \rightarrow \infty$

Carothers  $\bar{p}_n \rightarrow \infty$

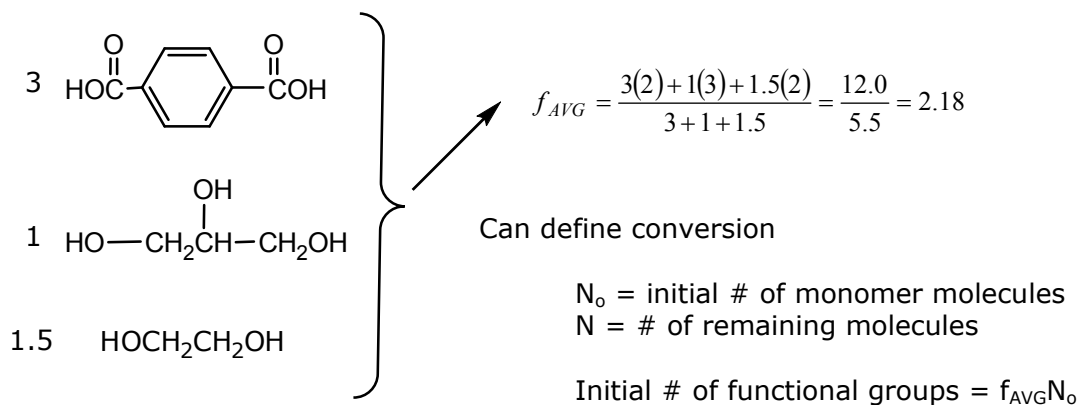
Consider simplest case:

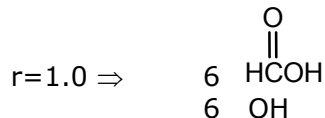
Equal # of a,b functional groups

$$\text{Define } f_{AVG} = \frac{\sum N_i f_i}{\sum N_i}$$

$f_i$  = functionality of given monomer  $f_i \geq 1.0$

$N_i$  = # of molecules with  $f_i$





# of functional groups reacted =  $2(N_o - N)$

For each a-b reaction, lose 1a, 1b  $\Rightarrow$  2 functional groups

For each a-b reaction, decrease # of molecules by 1

$$\text{(a)} \quad \pi = \frac{\text{\# of functional groups reacted}}{\text{total \# of functional groups}} = \frac{2(N_o - N)}{N_o f_{AVG}}$$

$$\text{(b)} \quad \bar{p}_n = \frac{N_o}{N} \quad (\text{see original definition})$$

# avg degree of polymerization

Rearrange (a):

$$N_o f_{AVG} \pi = 2N_o - 2N$$

$$N_o (\pi f_{AVG} - 2) = -2N$$

$$\frac{N_o}{N} = \frac{-2}{\pi f_{AVG} - 2}$$

$$\boxed{\bar{p}_n = \frac{N}{N_o} = \frac{2}{2 - \pi f_{AVG}}}$$

Universal expression  
Carothers Equation  
Works for all the cases, but  $f_{AVG}$   
must be adjusted when  $r \neq 1.0$

Rearrange Carothers:

$$\boxed{\pi = \frac{2}{f_{AVG}} - \frac{2}{\bar{p}_n f_{AVG}}}$$

Consider gel point:  $\bar{p}_n \rightarrow \infty$

$$\Rightarrow \pi_c = \frac{2}{f_{AVG}} \quad \left. \vphantom{\pi_c} \right\} \begin{array}{l} \pi \text{ at gel} \\ \text{point} \end{array} \quad \left. \vphantom{\pi_c} \right\} \begin{array}{l} \text{general expression} \\ \text{for Carothers} \end{array}$$

more functionality  $\rightarrow$  gel at lower conversion

e.g.  $f_{AVG} = 2.18$

$$\pi_c = \frac{2}{2.18} = 0.92$$

Consider less perfect case:

$$f_{AVG} = \frac{\sum N_i f_i}{\sum N_i} \quad \text{only true for } r = \frac{(Na)_o}{(Nb)_o} = 1.0$$

If  $r \neq 1.0 \Rightarrow$  only gain in increased MW + crosslinking when using -a + -b  
(i.e. deficient group quantity determines how many of these  
reactions take place)

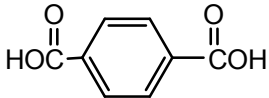
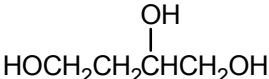
Excess of b only decreases  $\overline{p_n}$  by end capping  
 Count only a groups + 2


$$f_{AVG} = \frac{2(\sum N_i f_{ai})}{\sum N_i}$$

$f_{A,i}$  = function in - a of monomer i

$N_{A,i}$  = # of molecules of monomer i

Example:

		N	$f_i$
A	HOCH <sub>2</sub> CH <sub>2</sub> OH	2	$f_A = f_{a,i} = 2$
B		4	$f_B = f_{b,i} = 2$
C		1	$f_C = f_{a,i} = 3$

Enter body copy in Verdana 10. 8b, (7a) deficient where a = OH  
 b = 

$$f_{AVG} = \frac{2(N_a f_a + N_c f_c)}{N_a + N_b + N_c} = \frac{2((2)(2) + (1)(3))}{2 + 4 + 1} = 2.0$$

$$\pi_c = \frac{2}{2.0} = 1.0$$

Only at full conversion do you form network.

$\pi_c > 1.0 \Rightarrow$  physically impossible to create network

Case of exact stoichiometry: doesn't matter which is deficient.

Let  $N_B = 3.5$

$$\pi_c = \frac{2}{2.15} = 0.93$$

Other case:

Flory-Stockmayer

$$\overline{p_w} \rightarrow \infty$$

Generalized cases:

$$\pi_c = \frac{1}{\{r(f_{w,A} - 1)(f_{w,B} - 1)\}^{1/2}}$$

$$f_{w,A} = \frac{\sum_i f_{A,i}^2 N_{A,i}}{\sum_i f_{A,i} N_{A,i}}$$

where  $f_{w,i}$  can be  $\geq 1.0$

$$f_{w,B} = \frac{\sum_i f_{B,i}^2 N_{B,i}}{\sum_i f_{B,i} N_{B,i}}$$

$$r = \frac{\sum_i f_{A,i} N_{A,i}}{\sum_i f_{B,i} N_{B,i}} \leq 1.0$$

For our earlier example,  $\pi_c = 0.90$  ( $N_B = 3.5$ )

Carothers:  $\pi_c = 0.93$

Lower  $\pi_c$   
 $\rightarrow$  longest chains form more of  
infinite network