Step Growth Polymerization

2 functional groups: a,b → form new link c, may be a side product d

$$a\!-\!a + b\!-\!b \rightarrow a\!-\!c\!-\!b + d$$
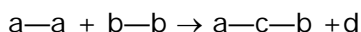
For example, if a—a is a diacid and b—b is a diol:

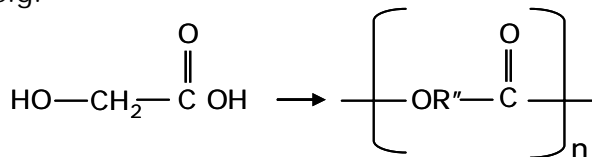Polyester
(one repeat unit consists of 2 structural units)
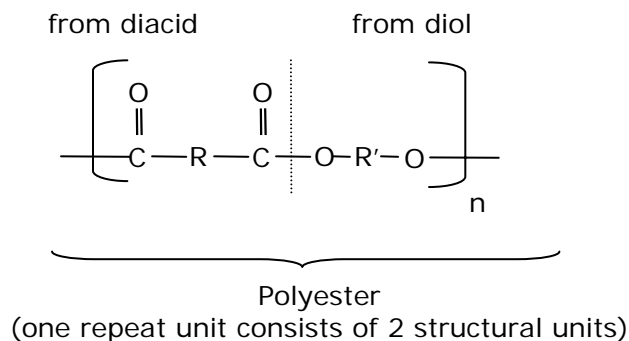
Degree of polymerization   ≡ number of monomer units or structural units incorporated in polymer chain
$$= \overline{p_n}$$

$$\overline{M_n} = \frac{\overline{p_n} \cdot M_u}{2} \quad \text{where } M_u = \text{molecular weight (MW) of individual repeat units}$$

Can also have a—b monomers:
      e.g.

In this case:
- $R'' = CH_2$
- The repeat unit is the structural unit
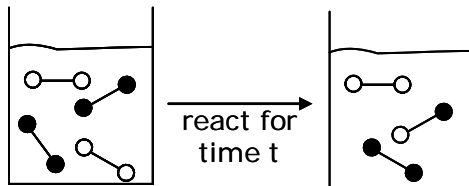$$\overline{M_n} = \overline{p_n} \cdot M_u$$

Determining MW as a Function of Conversion

How do you determine MW as a function of conversion?

$$\overline{p_n} = \frac{\text{total initial \# of monomer units}}{\text{total \# of molecules remaining}} = \frac{N_o}{N_{total}}$$

Simple thought experiment:

50 monomer units	{	25 a—a	○—○
		25 b—b	●—●

react for time t

If have 50% conversion $\Rightarrow$ 25 a+b reactions
$\Rightarrow$ lose molecule w/each reaction (2 molecules become 1)

$$\overline{p_n} = \frac{50}{50 - 25} = 2$$

So π (conversion) can be related to $\overline{p_n}$.

$(Na)_o$ = initial \# of a reactive group = 2 (\# of a-a monomers)
$(Nb)_o$ = initial \# of b reactive group = 2 (\# of b-b monomers)

$$\pi_a = 1 - \frac{Na}{(Na)_o} \qquad\qquad \pi_b = 1 - \frac{Nb}{(Nb)_o}$$

Define $r \equiv \dfrac{(Na)_o}{(Nb)_o} \leq 1$ Define: *a* is minority functional group
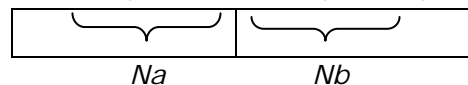
↑
Stoichiometric ratio

Total \# of functional groups initially present

$$N_o = (Na)_o + (Nb)_o = (Na)_o \left[1 + \frac{1}{r} \right]$$

At a given time t, have conversion π_a

N_t = \# of functional groups at time t = $(Na)_o (1 - \pi_a) + (Nb)_o - (Na)_o \pi_a$

$\underbrace{\qquad\qquad}_{Na} \underbrace{\qquad\qquad}_{Nb}$

$$N_t = (Na)_o \left(1 - 2\pi_a + \frac{1}{r}\right)$$

$$\therefore \quad \boxed{\overline{p_n} = \frac{\dfrac{N_o}{2}}{\dfrac{N_t}{2}} = \frac{N_o}{N_t} = \frac{1 + \dfrac{1}{r}}{1 - 2\pi_a + \dfrac{1}{r}} = \frac{1 + r}{1 - 2\pi r + r}}$$

$$\pi_a = \pi \quad \text{(assume referring to minority)}$$

Simple case: r = 1.0 (perfect stoichiometry)

At					
	$\pi = 0.995^*$	$\rightarrow$	$\overline{p_n} = 200$		
	$\pi = 0.99$	$\rightarrow$	$\overline{p_n} = 100$	$\overline{p_n}$ drops fast	
	$\pi = 0.98$	$\rightarrow$	$\overline{p_n} = 50$		
	$\pi = 0.90$	$\rightarrow$	$\overline{p_n} = 10$	oligomer	

*Can take a long time. First 95% takes same time as last 2-3%.

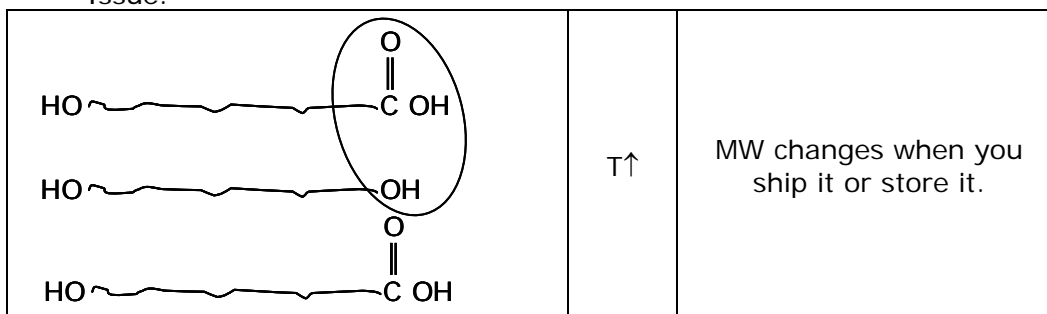Must ↑ π to get high MW $\overline{p_n} = \dfrac{1}{1 - \pi}$ As π ↑, $\overline{p_n}$ explodes.

But, there is a problem:

Control of MW

How to control MW?

       a) Control π (conversion)

          Issue:

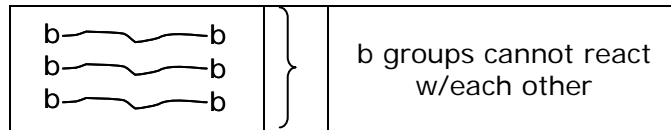|		
(structures: HO~~C OH, HO~~OH, HO~~C OH)	T↑	MW changes when you ship it or store it.

       b) Control stoichiometry:

          Assume: e.g. π = 1.0

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

       Add excess of b—b

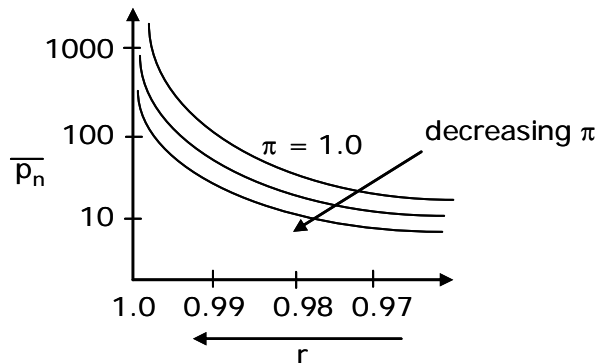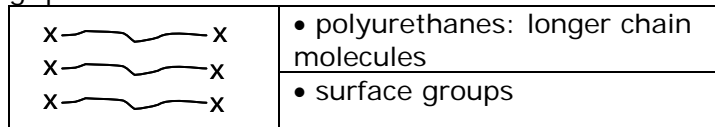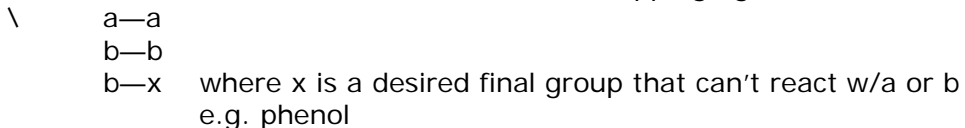   End up "capping" chains w/b groups

b———b b———b b———b	b groups cannot react w/each other

e.g. 1% excess of b-b

$\Rightarrow$ max $\overline{p_n} = 199$

Can intentionally cap w/alcohol or ester for certain applications.

Can use π, r to predict MW outcome of rxn.

Can also use monofunctional unit as an end capping agent:

\   a—a

        b—b

        b—x   where x is a desired final group that can't react w/a or b

               e.g. phenol

x———x x———x x———x	• polyurethanes: longer chain molecules • surface groups

Here we redefine the ratio r:

Assume a—a b—b are in equal quantity		$r = \dfrac{(Na)_o}{(Nb)_o + 2N_x}$ where N_x = # of b-x molecules		Caveat: $(Na)_o = (Nb)_o$ a—a b—b for this to work.

Same expression if you're using a—b monomers.

MW Distribution as a Function of Conversion:

Assumptions: 1. Equal reactivities for all a,b functional groups.
            Reactivities are the same for short a—a and long polymer
            (length independence) in viscous fluid.
            2. Perfect stoichiometry: r = 1
            3. For ease of explanation, use a-b monomer ($\pi_a = \pi_b$).

At a given time t, have conversion π

        Probability that an a group has reacted: $p = \pi$

(will use p, π interchangeably)
Probability that a molecule has x structural units = $\wp_x$

x structural units $\Rightarrow$	(x-1) =	# of a groups reacted		Prob of this combination
	1	a group unreacted		

Prob of x-1 a groups reacted: p^{x-1}
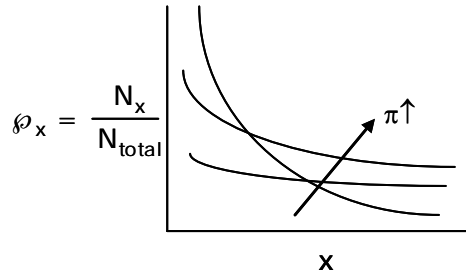Prob of unreacted a: $(1-\pi)$ or $(1-p)$

So, $\wp_x = p^{x-1}(1-p)$

$\wp_x$ = number fraction of chains with degree of polymerization x

$$\wp_x = \frac{\text{\# of x-length chains}}{\text{total \# of chains}} = \frac{N_x}{N_{total}} = \frac{N_x}{N_o(1-p)} = \frac{N_x}{N_o - N_o p}$$

Every time a molecule
reacts lose $N_o p$.

$N_x = \wp_x N_o (1-p)$

$$\wp_x = \frac{N_x}{N_{total}}$$

$\pi\uparrow$

x

increase conversion $\rightarrow$ narrower and broader

Flory-Shulz Distribution: Some Monomer Always Present

$$\overline{p_n} = \frac{\sum_x x N_x}{\sum_x N_x} = \sum x \wp_x = \sum x p^{x-1}(1-p)$$

$$\sum p^{x-1} = \frac{1}{1-p}$$

$$\sum x p^{x-1} = \frac{1}{(1-p)^2}$$

$$\overline{p_n} \Rightarrow \frac{1}{(1-p)}$$

Weight fraction: $\quad w_x = \dfrac{xN_x}{N_o} = x(1-p)^2\, p^{x-1}$

$\overline{p_w} = \dfrac{1+p}{1-p}\ \text{ or }\ \dfrac{1+\pi}{1-\pi}$

Result of using $\overline{p_w}$
expression and summations

$\text{PDI} = z = \dfrac{\overline{p_w}}{\overline{p_n}} = 1+p = 1+\pi$

As $\qquad \pi \to 1.0$
$\qquad\qquad z \to 2.0$

increasing π

w_x

x