

# Chapter 10.

## Step-Reaction and Ring-Opening Polymerization

### 10.2. Step-Reaction Polymerization - Kinetics

#### Step-Reaction Polymerization

1. **Difunctional** monomers  $\rightarrow$  **Linear** polymers  
AB type, AA and BB
2. **Polyfunctional** monomers  $\rightarrow$  **Network** polymers  
Functionality  $> 2$
3. Polymers retain their **functionality** as **end groups**  
at the completion of polymerization
4. **Single reaction** (cf. initiation, propagation, and termination  
in chain-reaction polymerization)

5. M.W. increases **slowly**

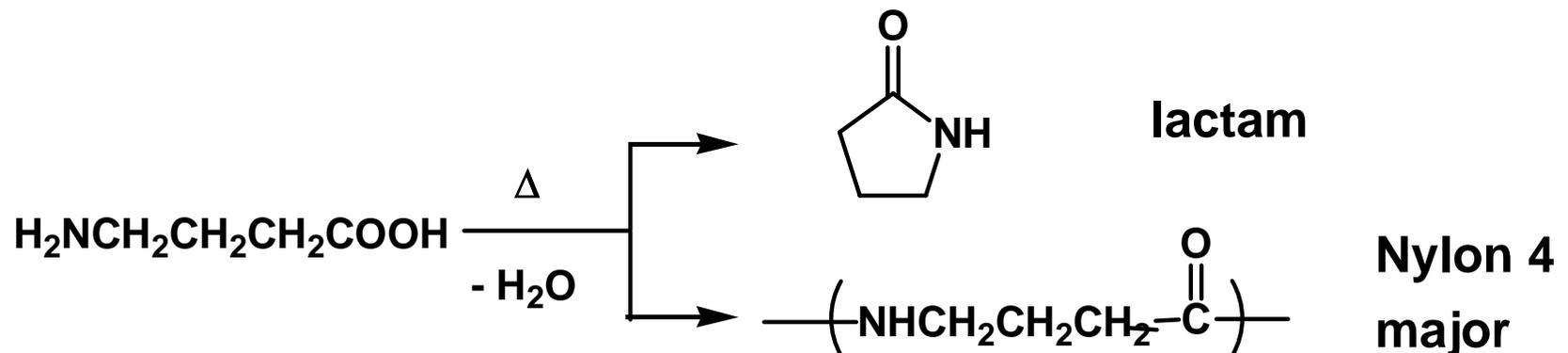
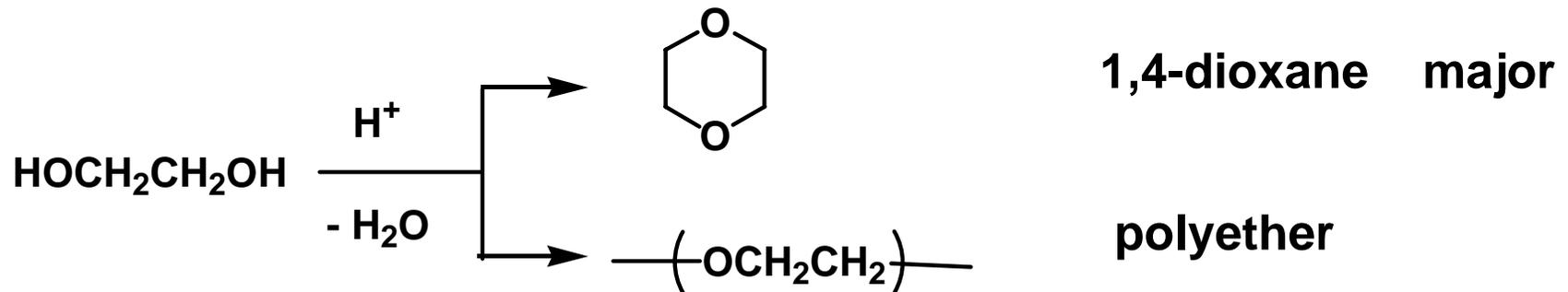
**Carothers** equation

$$\overline{DP} = \frac{1}{1-p}$$

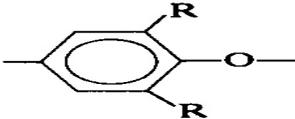
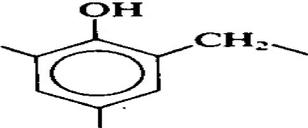
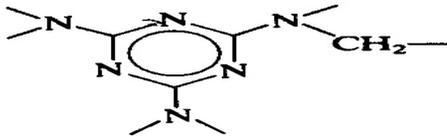
$p$  = extent of reaction

6. **High-yield reactions** and an **exact stoichiometric balance** are necessary to obtain **high-m-w linear polymer**

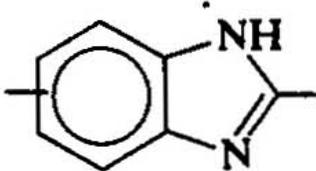
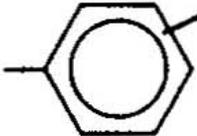
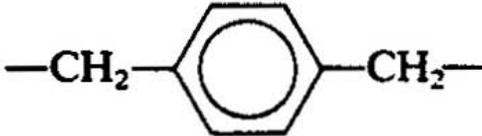
7. Formation of **cyclic byproduct**



**TABLE 10.1.** Commercially Important Polymers Prepared by Step-Reaction Polymerization

| <i>Polymer Type</i>                | <i>Repeating Functional Unit</i>                                                     | <i>Chapter</i> |
|------------------------------------|--------------------------------------------------------------------------------------|----------------|
| Polyether                          | $-\text{Ar}-\text{O}-$                                                               | 11             |
| Polyether [poly(phenylene oxide)]  |    | 11             |
| Polyether (epoxy) <sup>a</sup>     | $-\text{CH}_2\overset{\text{OH}}{\text{C}}\text{HCH}_2\text{OAr}-$                   | 11             |
| Polysulfide                        | $-\text{ArS}-$                                                                       | 11             |
| Poly(alkylene polysulfide)         | $-\text{RS}_x-$                                                                      | 11             |
| Polysulfone                        | $-\text{ArSO}_2-$                                                                    | 11             |
| Polyester                          | $-\overset{\text{O}}{\parallel}\text{RCO}-$                                          | 12             |
| Polycarbonate                      | $-\overset{\text{O}}{\parallel}\text{ROCO}-$                                         | 12             |
| Polyamide                          | $-\overset{\text{O}}{\parallel}\text{RCNH}-$                                         | 13             |
| Polyurea                           | $-\text{RNHC}\overset{\text{O}}{\parallel}\text{NH}-$                                | 13             |
| Polyurethane                       | $-\text{ROC}\overset{\text{O}}{\parallel}\text{NH}-$                                 | 13             |
| Phenol-formaldehyde <sup>b</sup>   |   | 14             |
| Urea-formaldehyde <sup>c</sup>     | $\text{N}\overset{\text{O}}{\parallel}\text{C}\text{NHCH}_2-$                        | 14             |
| Melamine-formaldehyde <sup>b</sup> |  | 14             |
| Polyimide                          | $-\text{Ar}-\overset{\text{O}}{\parallel}\text{N}-$                                  | 15             |

**TABLE 10.1.** (continued)

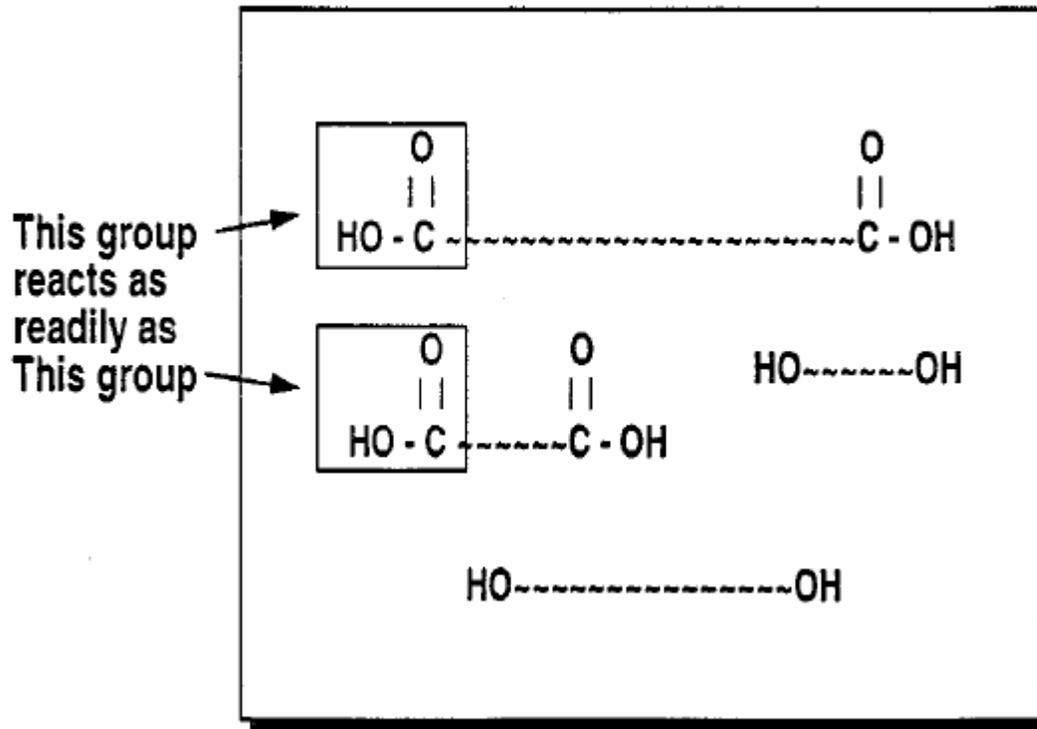
| <i>Polymer Type</i>       | <i>Repeating Functional Unit</i>                                                     | <i>Chapter</i> |
|---------------------------|--------------------------------------------------------------------------------------|----------------|
| Polybenzimidazole         |    | 15             |
| Polyphenylene             |   | 17             |
| Poly( <i>p</i> -xylylene) |  | 17             |

# Kinetics of Step-Growth Polymerization

## Flory's assumption

The **reactivity** of a functional group is **independent** of the **length** of the chain to which it is attached.

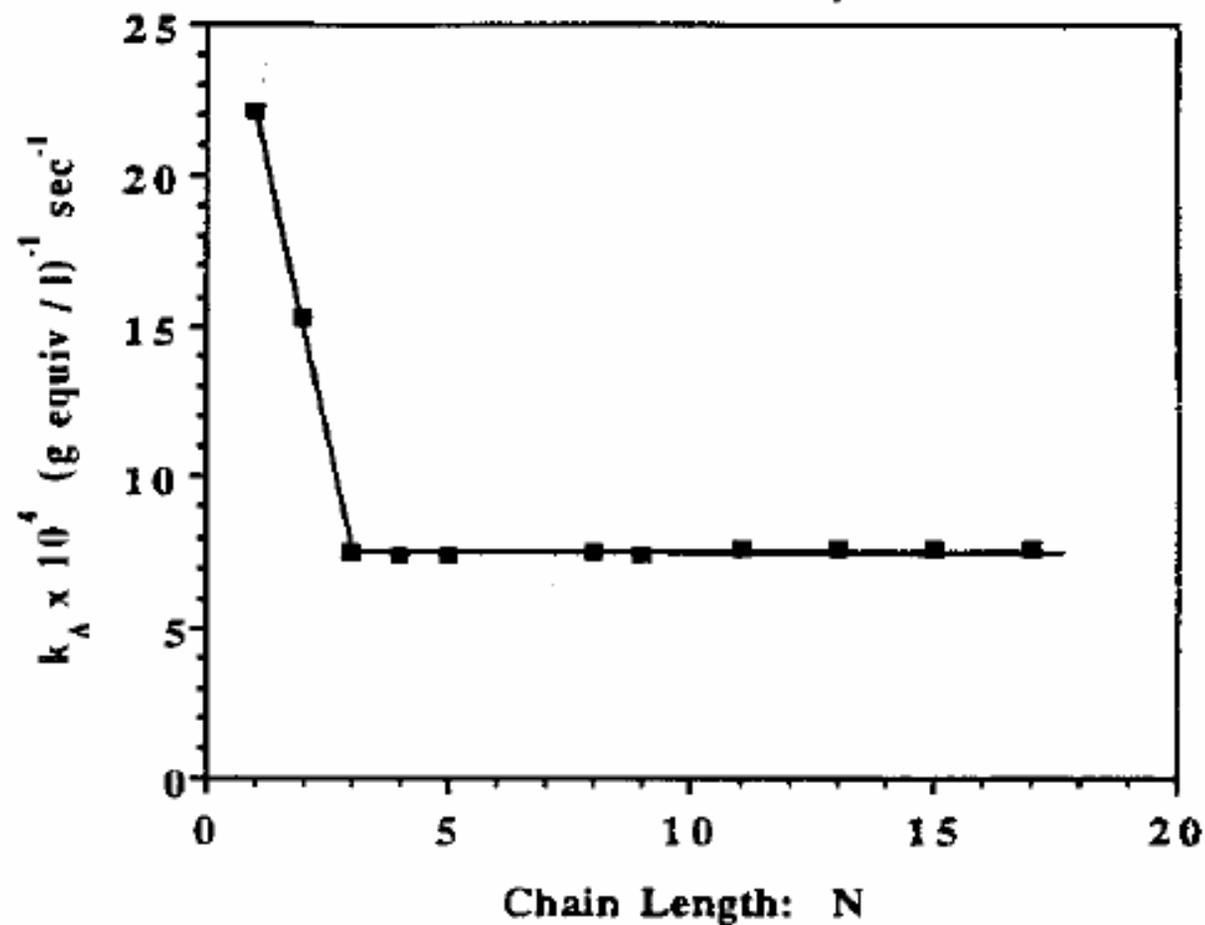
*Example: dibasic acid + glycol polyester*



### *Assumption 2.*

- The **reactivity** of a functional group is unaffected by **reactions** of other functional groups in the molecule

# WAS FLORY RIGHT?



The **probability of chemical reaction** with the increase of the MW:

- The **rate of molecular diffusion decreases**, i.e., larger time intervals between encounters (fewer encounters of functional groups per unit time)
- **Greater duration of each encounter** (a larger number of collisions of functional groups per encounter)

- **Kinetics**

1. **Catalyzed**

$$[\text{cat}]k' = k$$

**[cat]** is **unchanged**

If polymerization reaction is **first order**  
w.r.t. each functional group (A & B)

**Polymerization rate**

$$-\frac{d[A]}{dt} = k[A][B]$$

$$\frac{1}{[A]_0(1-p)} - \frac{1}{[A]_0} = kt$$

If **[A] = [B]**

$$-\frac{d[A]}{dt} = k[A]^2$$

$$\frac{\overline{DP}}{[A]_0} - \frac{1}{[A]_0} = kt$$

or

$$\overline{DP} = [A]_0 kt + 1$$

$$t = \frac{\overline{DP} - 1}{[A]_0 k}$$

By **integration**

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$\overline{DP} = \frac{[A]_0}{[A]} = \frac{1}{1-p}$$

If **k** is known, **time** can be calculated.

## 2. Uncatalyzed (self-catalyzed)



Carboxylic acid: role of catalyst

$$-\frac{d[A]}{dt} = k[A]^2[B]$$

Assume  $[A] = [B]$

$$-\frac{d[A]}{dt} = k[A]^3$$

Integration

$$\frac{1}{[A]^2} - \frac{1}{[A]_0^2} = 2kt$$

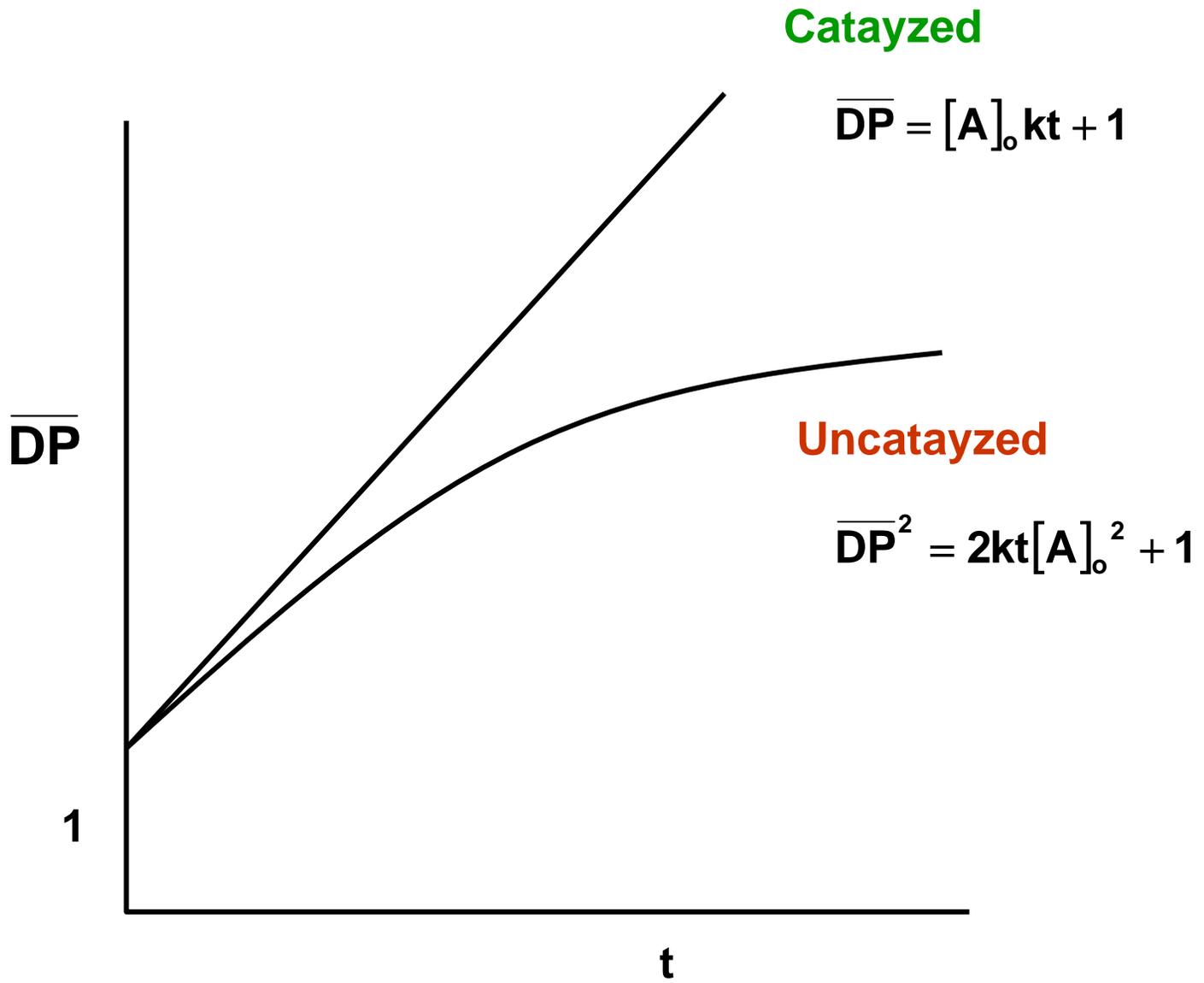
$$[A] = [A]_0(1 - p)$$

$$\frac{1}{[A]_0^2(1-p)^2} - \frac{1}{[A]_0^2} = 2kt$$

$$\frac{1}{(1-p)^2} = 2kt[A]_0^2 + 1$$

$$\overline{DP}^2 = 2kt[A]_0^2 + 1$$

M.W. increases **more gradually** than when acid catalyst is added.



## 10.3 Stoichiometric Imbalance

- Three ways **to limit M.W.** in step polymerization
  1. To **quench** the polymerization reaction by rapid cooling when the desired M.W. is attained.
  2. To use an **excess** of one monomer.
  3. To use small amounts of **monofunctional reactant**

- Stoichiometric imbalance factor

$$r = \frac{N_A^\circ}{N_B^\circ}$$

where

$N_A^\circ$  = initial # of **A** functional groups

$N_B^\circ$  = initial # of **B** functional groups

By convention

$$r \leq 1$$

$$p = \text{extent of reaction} = \frac{N_A^\circ - N_A}{N_A^\circ}$$

$$N_A = (1 - p)N_A^\circ$$

$$N_B = (1 - pr)N_B^\circ = (1 - pr)\frac{N_A^\circ}{r}$$

# of molecular chains at  $p$

$$\begin{aligned} N &= \frac{1}{2}(N_A + N_B) \\ &= \frac{1}{2}\left[(1 - p)N_A^\circ + (1 - pr)\frac{N_A^\circ}{r}\right] \\ &= \frac{N_A^\circ}{2}\left(1 + \frac{1}{r} - 2p\right) \end{aligned}$$

cf.  $N_B = N_B^\circ - pN_A^\circ = N_B^\circ - prN_B^\circ$

## # monomers

$$N^{\circ} = \frac{1}{2} (N_A^{\circ} + N_B^{\circ})$$

Since  $r = \frac{N_A^{\circ}}{N_B^{\circ}}$

$$N^{\circ} = \frac{1}{2} \left( N_A^{\circ} + \frac{N_A^{\circ}}{r} \right) = \frac{N_A^{\circ}}{2} \left( \frac{r+1}{r} \right)$$

## Average degree of polymerization

$$\overline{DP} = \frac{N^{\circ}}{N} = \frac{\frac{N_A^{\circ}}{2} \left( \frac{r+1}{r} \right)}{\frac{N_A^{\circ}}{2} \left( 1 + \frac{1}{r} - 2p \right)} = \frac{1+r}{1+r-2rp}$$

If  $r = 1$

$$\overline{DP} = \frac{1}{1-p}$$

If  $p = 1$

$$\overline{DP} = \frac{1+r}{1-r}$$

If **monofunctional reagent** is added

**Imbalance factor**

$$r' = \frac{N_A^{\circ}}{N_B^{\circ} - 2N_{B'}^{\circ}}$$

where

$N_B^{\circ}$  = # of monofunctional B groups

**Factor 2** : each **B' molecule** is equally as effective as **one excess BB monomer** in limiting the M.W.

## 10.4 M.W. Distribution

# of **total molecules** at  $p = N$

# of **x-mers** =  $N_x$

$$M - (M)_{x-2} - M$$

$p \quad p \quad 1 - p$

where

$p$  = extent of reaction = **probability of reaction**  
 $1 - p$  = probability of finding an **unreacted** group

$$N_x = Np^{x-1}(1-p)$$

$$\frac{N}{N_0} = 1 - p \quad N_0 = \text{initial \# of monomers}$$

$$N_x = N_0(1-p)^2 p^{x-1}$$

$n_x$  = **mole fraction** of x-mers

$$n_x = \frac{N_x}{N} = (1-p)p^{x-1}$$

$$p = 0.99$$

**Monomer: the most abundant species**

**Wt fraction of x-mers**

$$w_x = \frac{xN_x M_o}{N_o M_o} = \frac{xN_x}{N_o} \quad \text{cf.} \quad N_x = N_o (1-p)^2 p^{x-1}$$

where  $M_o$  = mass of repeating unit

**Wt fraction distribution**

$$w_x = (1-p)^2 x p^{x-1}$$

**The most abundant species**

$$\begin{aligned} \frac{dw_x}{dx} &= (1-p)^2 p^{x-1} + (1-p)^2 x p^{x-1} \ln p \\ &= (1-p)^2 p^{x-1} (1 + x \ln p) = 0 \quad \longrightarrow \quad x = -\frac{1}{\ln p} \end{aligned}$$

$$\overline{M}_n = \sum n_x M_x = \sum n_x x M_o = M_o (1-p) \sum x p^{x-1} = M_o (1-p) \frac{1}{(1-p)^2} = \frac{M_o}{1-p}$$

$$\text{cf. } \sum_{x=1}^{\infty} x p^{x-1} = \frac{1}{(1-p)^2}$$

$$\overline{M}_w = \sum w_x M_x = \sum w_x x M_o = M_o (1-p)^2 \sum x^2 p^{x-1} = M_o (1-p)^2 \frac{1+p}{(1-p)^3} = \frac{M_o (1+p)}{1-p}$$

$$\text{cf. } \sum_{x=1}^{\infty} x^2 p^{x-1} = \frac{1+p}{(1-p)^3}$$

**Polydispersity index**

$$\frac{\overline{M}_w}{\overline{M}_n} = 1 + p$$

$$\text{As } p \rightarrow 1, \quad \frac{\overline{M}_w}{\overline{M}_n} \rightarrow 2$$

Fig 10.1 Mole fraction distribution in linear step-reaction polymerization

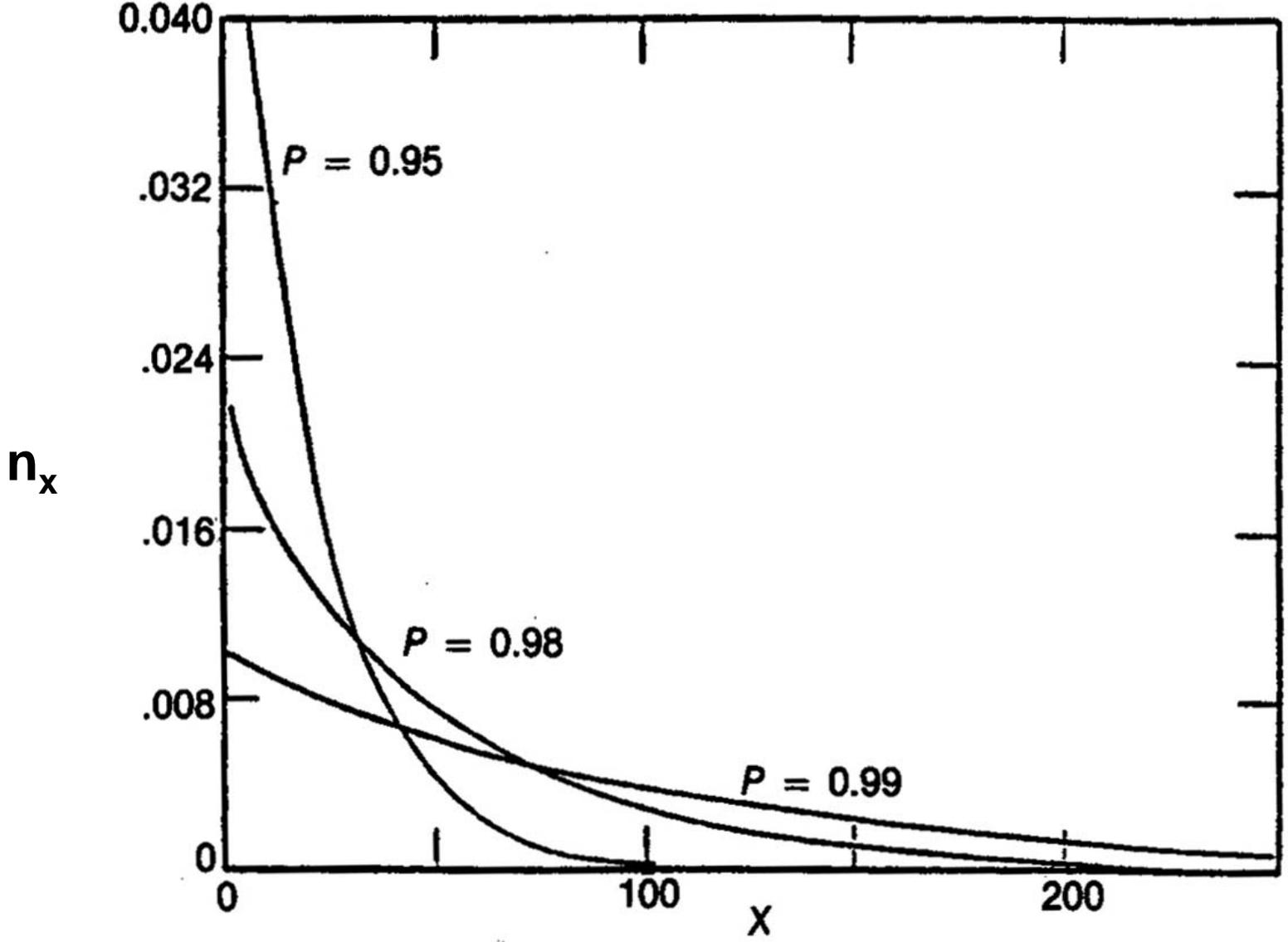
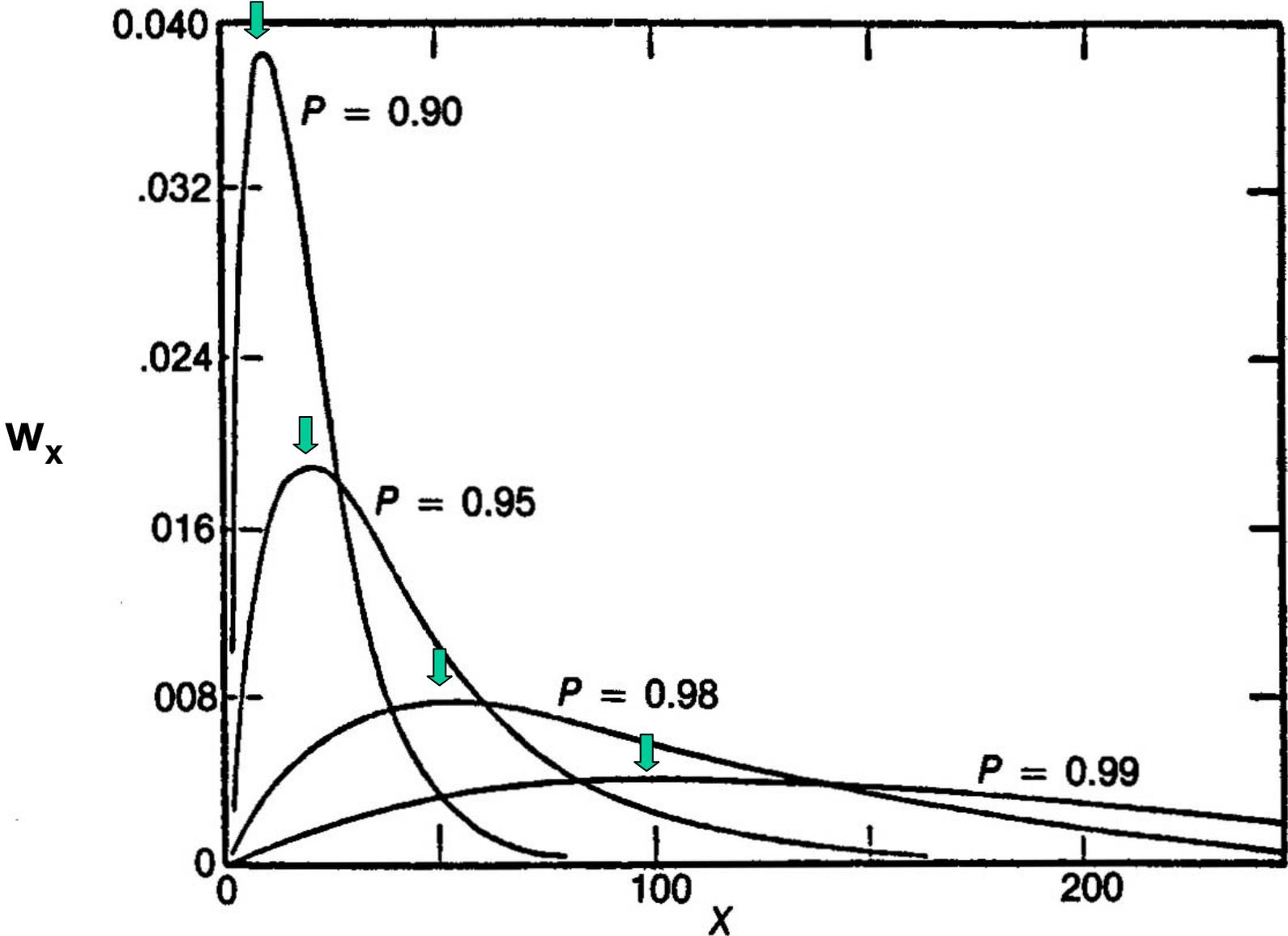
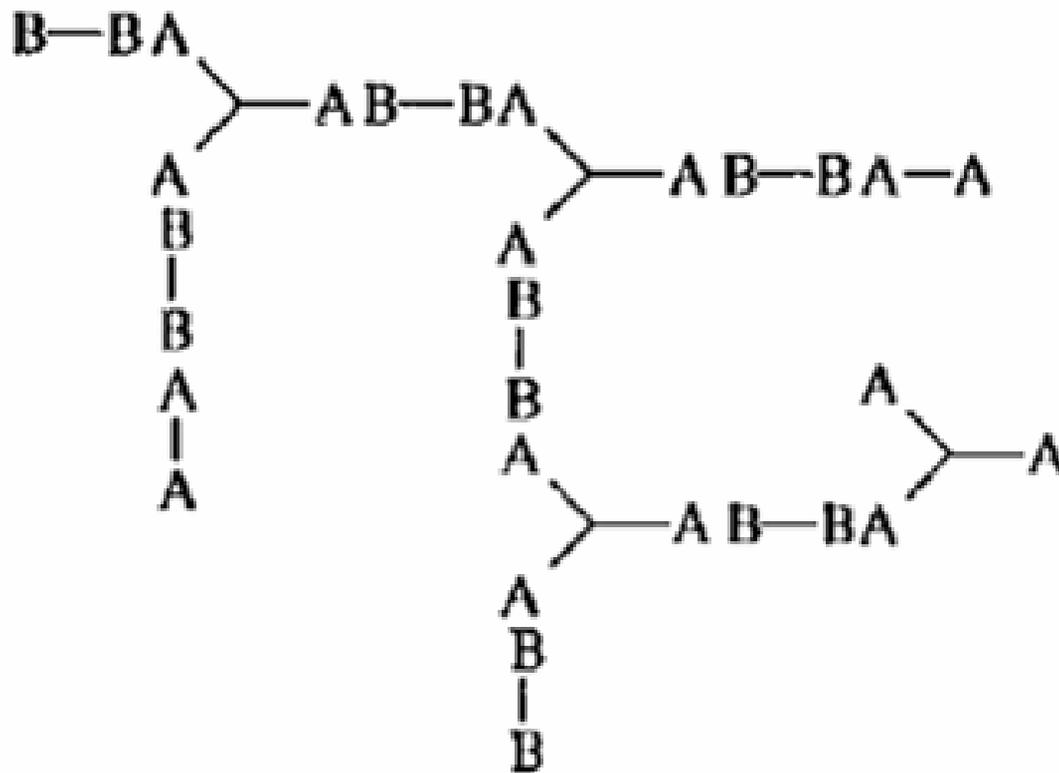
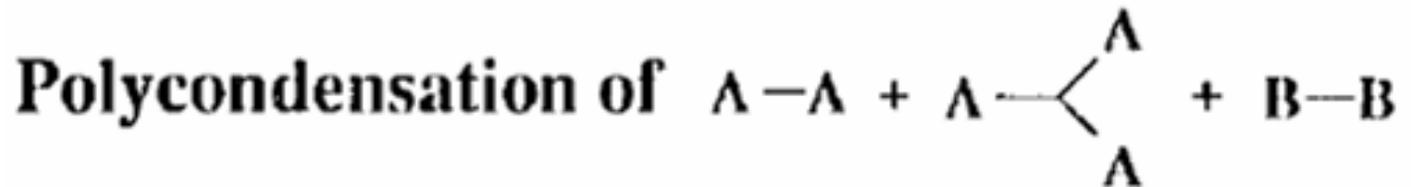


Fig 10.2 Weight fraction distribution in linear step-reaction polymerization

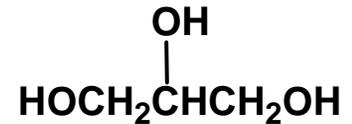
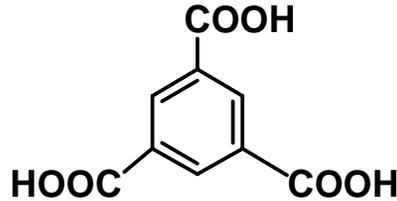
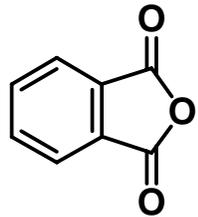


# Theory of Gelation



## 10.5 Network Step Polymerization

Equimolar mixture



Functionality

2

3

2

3

Average functionality

$$f_{av} = \frac{2 + 3 + 2 + 3}{4} = 2.5$$

$N_o$  = initial # of monomers

$N$  = # of molecules at  $p$

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

Initial # of functional groups =  $N_o f_{av}$

$$p = \frac{2(N_o - N)}{N_o f_{av}} = \frac{2}{f_{av}} - \frac{2N}{N_o f_{av}} = \frac{2}{f_{av}} - \frac{2}{\overline{DP} f_{av}} \quad \text{cf.} \quad \overline{DP} = \frac{N_o}{N}$$

At gel point  $\overline{DP} = \infty$

$$p_c = \frac{2}{f_{av}} \quad \text{Critical extent of reaction}$$

If  $f_{av} = 2.5$ ,  $p_c = 80\%$  (cf: difunctional monomers :  $\overline{DP} = 5$ )

If mixture 3 mol of 1, 2 mol of 4

$$f_{av} = \frac{(3 \times 2) + (2 \times 3)}{5} = 2.4$$

$$p_c = \frac{2}{2.4} = 83\%$$

|                | A - A              | B - B              | A <sub>f</sub>         |
|----------------|--------------------|--------------------|------------------------|
| # of molecules | N <sub>A</sub>     | N <sub>B</sub>     | N <sub>C</sub>         |
| Functionality  | f <sub>A</sub> = 2 | f <sub>B</sub> = 2 | f <sub>C</sub> = f > 2 |

### Imbalance factor

$$r = \frac{f_A N_A + f_C N_C}{f_B N_B} = \frac{2N_A + f_C N_C}{2N_B}$$

$$\rho = \frac{f_C N_C}{f_A N_A + f_C N_C} = \frac{f_C N_C}{2N_A + f_C N_C}$$

$p_A$  = extent of reaction for A

$p_B$  = extent of reaction for B =  $r p_A$

$$A_{f-1} - A - [B - B A - A]_i - B - B A - A_{f-1}$$

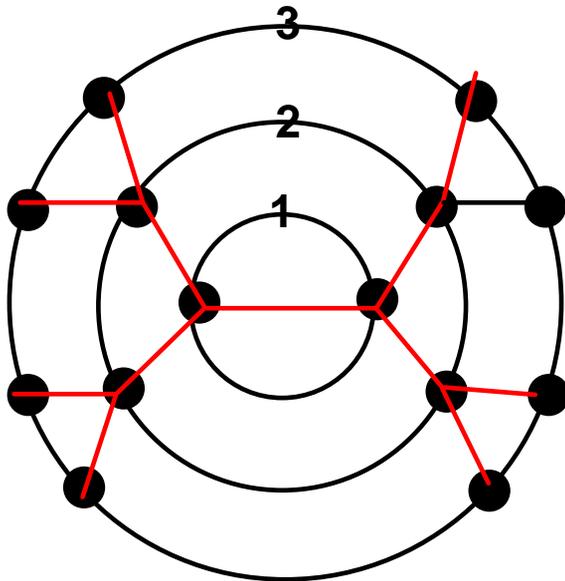
$$p_A (p_B(1 - \rho)p_A)^i \quad p_B \rho$$

$$= (r(1 - \rho)p_A^2)^i \quad = r\rho p_A$$

## Branching probability

= probability that a functional group on a **branch unit** leads to **another branch unit**

$$\alpha = \sum_{i=0}^{\infty} p_A [r(1 - \rho)p_A^2]^i r\rho p_A = \frac{r\rho p_A^2}{1 - r(1 - \rho)p_A^2}$$



## Trifunctionally branched network polymer

$i$  th envelope

$Y_i$  branch points on the  $i$  th envelope

# of branch points on  $(i + 1)$  th envelope

$$Y_{i+1} = 2 Y_i \alpha$$

### Criterion for gelation

$$Y_{i+1} > Y_i$$

$$2 Y_i \alpha > Y_i \quad \text{that is} \quad \alpha > \frac{1}{2}$$

$$\alpha_c = \frac{1}{2}$$

generally

$$\alpha_c = \frac{1}{f - 1}$$

$$\alpha_c = \text{critical branching probability} = \frac{1}{f-1}$$

$$\frac{1}{f-1} = \frac{r\rho p_c^2}{1-r(1-\rho)p_c^2}$$

$$1 - r(1-\rho)p_c^2 = (f-1)r\rho p_c^2$$

$$1 = (r - r\rho + fr\rho - r\rho)p_c^2$$

$$p_c = \frac{1}{[r + (f-2)r\rho]^{\frac{1}{2}}}$$

If  $r = 1$

$$p_c = \frac{1}{[1 + (f-2)\rho]^{\frac{1}{2}}}$$

If  $\rho = 1$

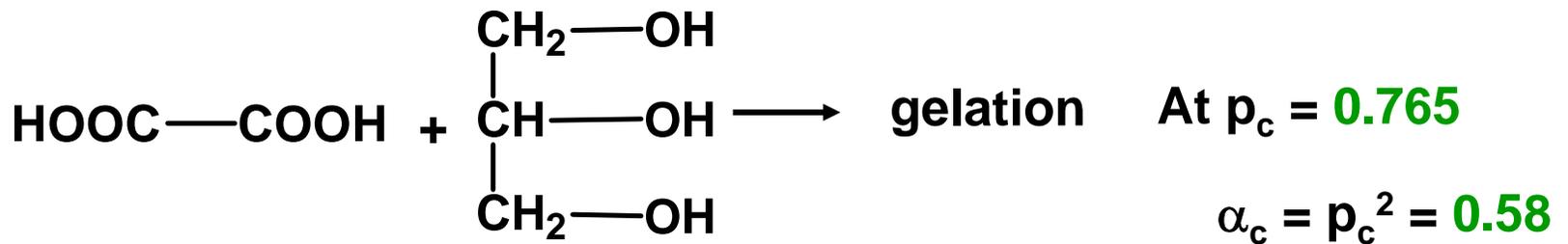
No A - A

All  $A_f$

$$p_c = \frac{1}{[(f-1)r]^{\frac{1}{2}}}$$

If  $r = \rho = 1$

$$p_c = \frac{1}{(f-1)^{\frac{1}{2}}}$$



### Theoretical (statistical)

$$p_c = \frac{1}{(3-1)^{\frac{1}{2}}} = \frac{1}{\sqrt{2}} = 0.707$$

$$\alpha_c = p_c^2 = \frac{1}{f-1} = \frac{1}{2}$$

### Carothers equation (nonstatistical)

$$f_{av} = \frac{(3 \times 2) + (2 \times 3)}{5} = 2.4$$

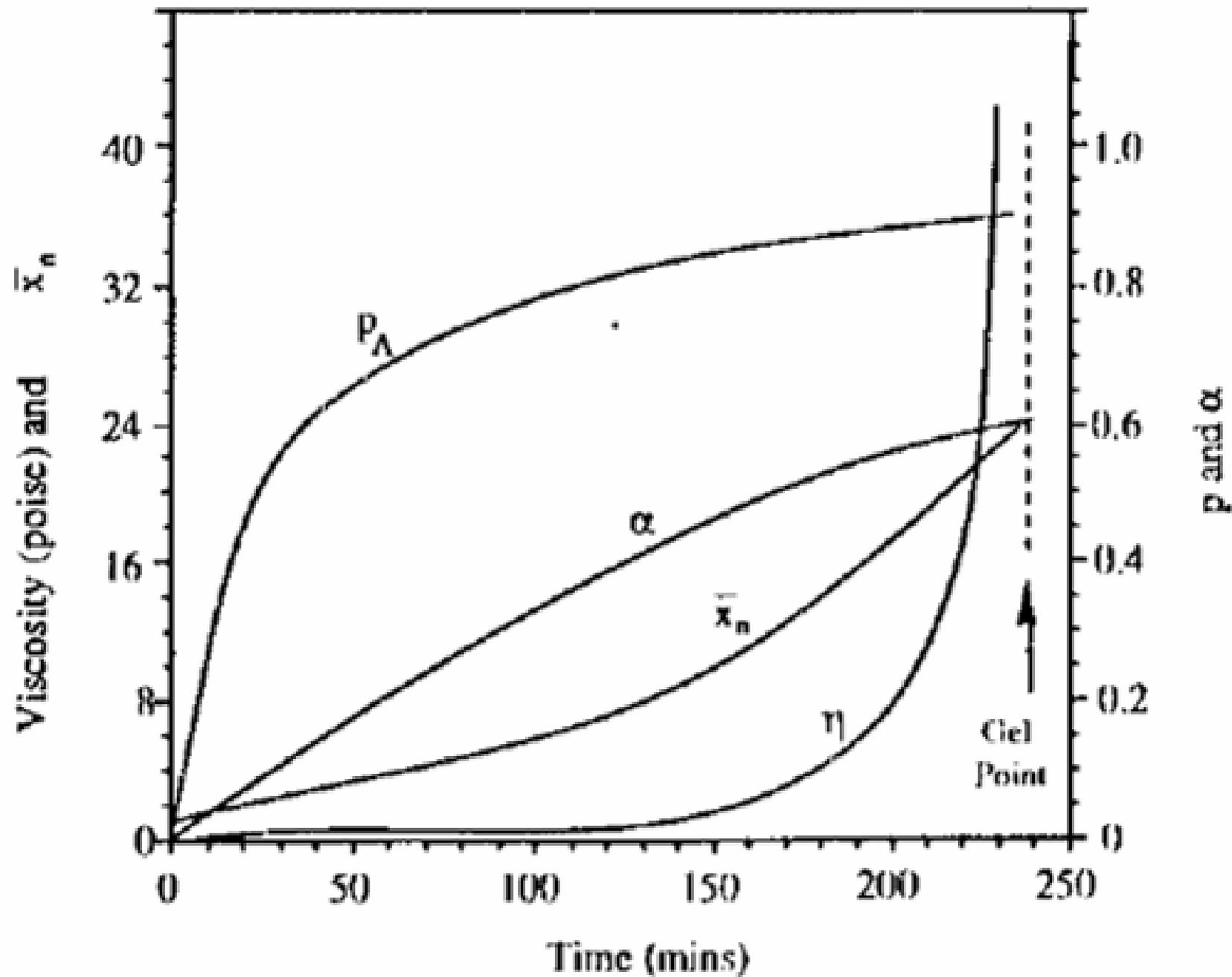
$$p_c = \frac{2}{f_{av}} \quad p_c = \frac{2}{2.4} = 83\%$$

Experimental values of  $p_c$  fall between the values calculated by statistical and nonstatistical methods.

### Deviation from statistical method

- ∴ (1) **Intramolecular branching reactions** leading to wasted loops
- (2) **Differing reactivities** of the functional groups

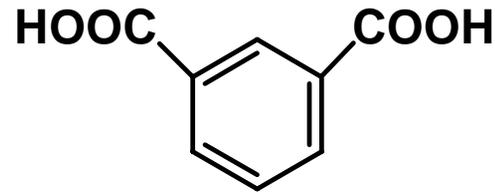
Reactivity of **secondary** alcohol < Reactivity of **primary** alcohol  
In glycerol



## 10.6 Step-Reaction Copolymerization



AA



BB

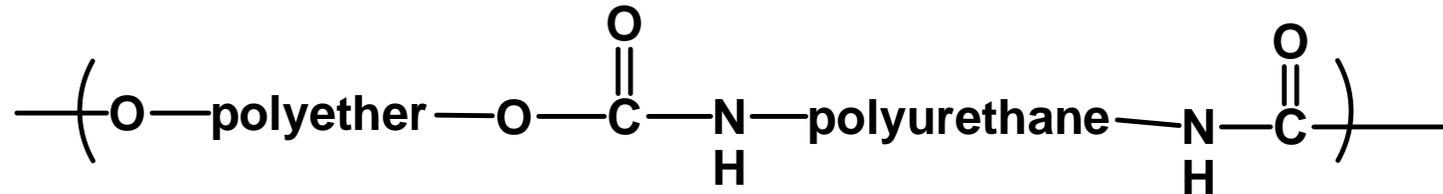


CC

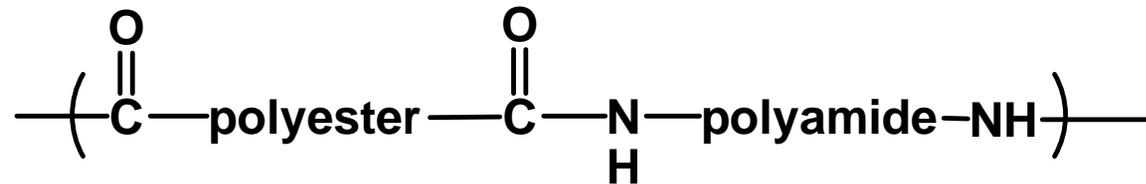
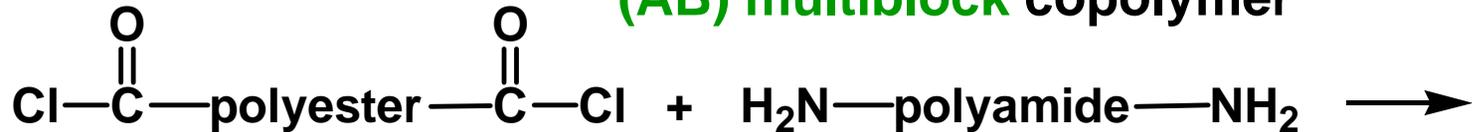
AA : BB : CC = 1 : 1 : 2     $\Rightarrow$     **Random** copolymer

AA + 2 CC  $\Rightarrow$  CC - AA - CC     $\Rightarrow$     **BB**  
- (CC - AA - CC - BB) -  
**Alternating** copolymer

## Step polymers : true telechelic polymers



(AB) multiblock copolymer



ABA triblock copolymer

## 10.7 Step Polymerization Techniques

### 1) **Bulk** polymerization

**Free of contaminants**

Disadvantage: **high viscosity**; **elevated temp** for effective **stirring** and **removal** of byproducts

**High vacuum** to remove byproducts

### 2) **Solvent** polymerization

**Low viscosity**

Removal of byproduct by **azeotropic distillation**

Removal of water in situ by use of effective **dehydrating agent**

Necessity of **removing solvent**

### 3) **Interfacial** polymerization

Solutions of **two monomers** in **separate, immiscible solvents**  
(one usually **water**)

Polymer is formed at the **interface**

e.g., Schotten – Baumann synthesis

“nylon rope trick”

**Rapid stirring** to **maximize the interfacial area** increases the yield of polymer

#### **Characteristics** of interfacial polymerization

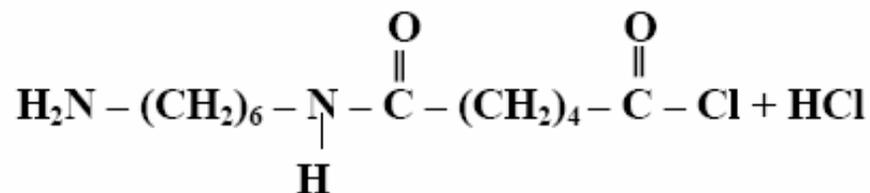
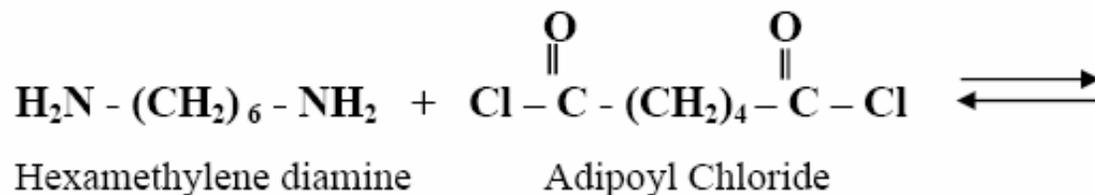
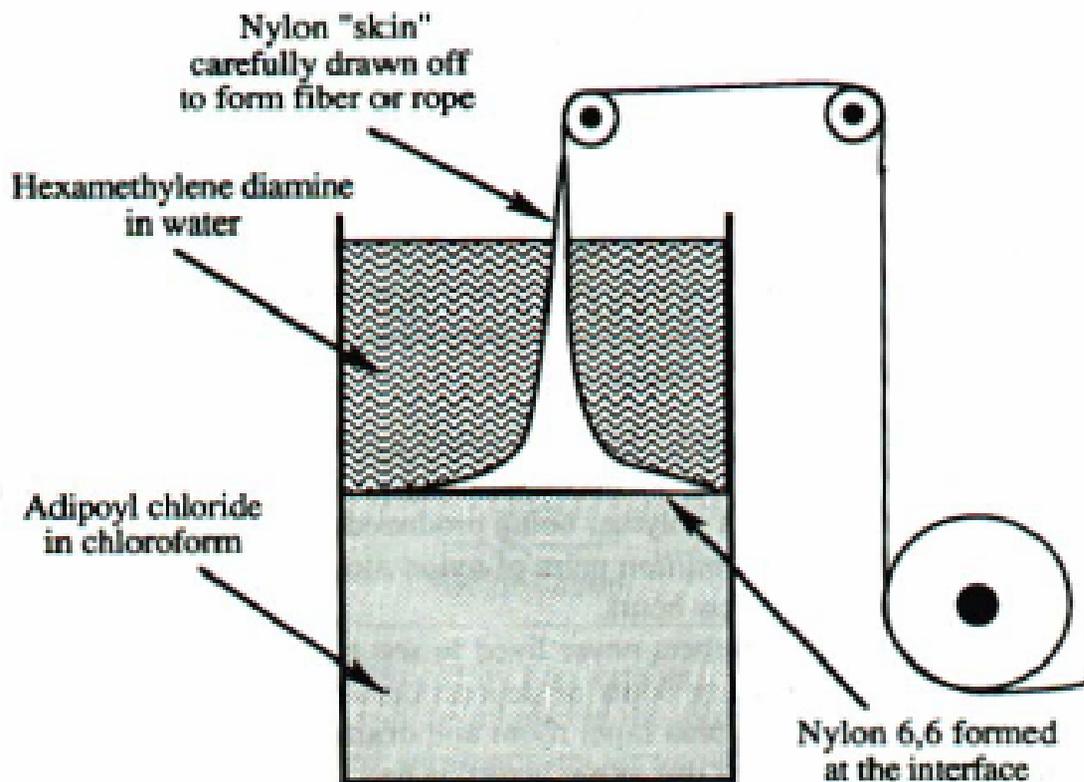
(1) Reaction goes **rapidly at low temp.**

(2) Reaction is so rapid, **diffusion of monomer** to the interface is **rate determining**

(3) **Monomer reacts with the growing chains** at the interface more rapidly **than** it diffuses through the polymer film to **initiate new chains**; hence **M.W.s** tend to be significantly **higher**.

(4) An exact **stoichiometric balance** is **not necessary**.

# Interfacial polymerization: the “nylon rope trick”

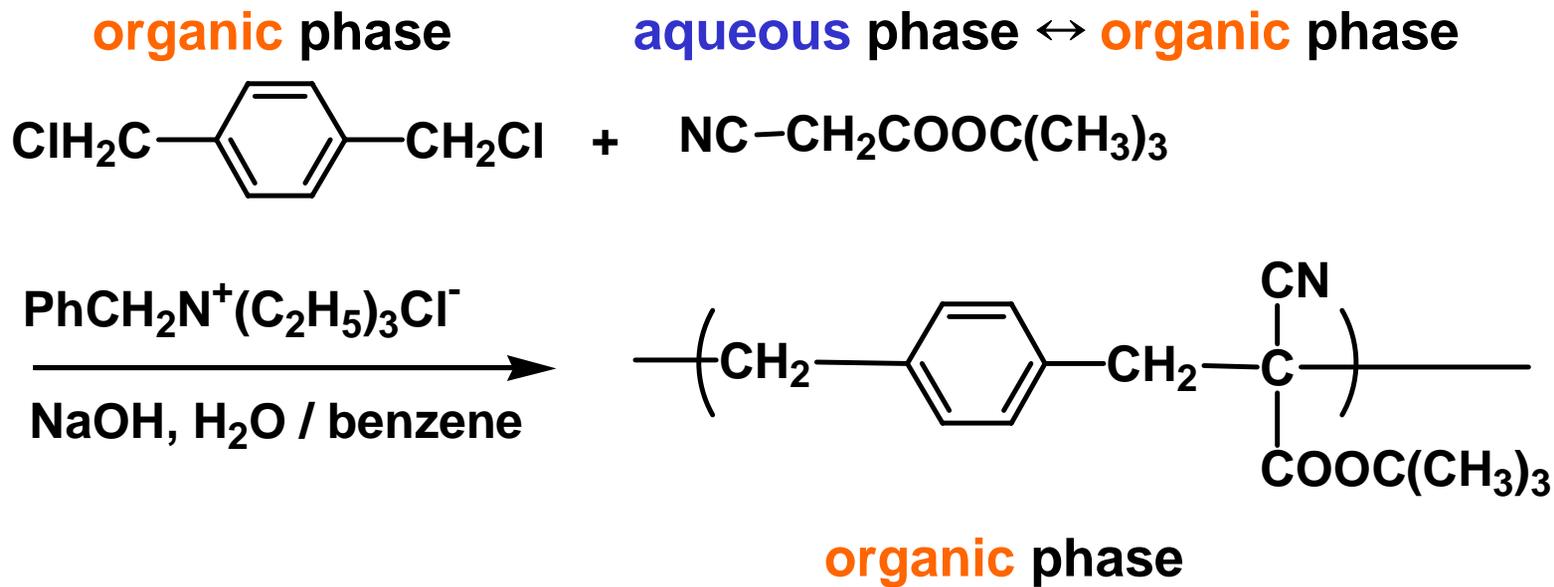


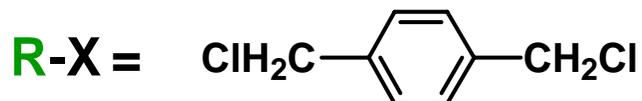
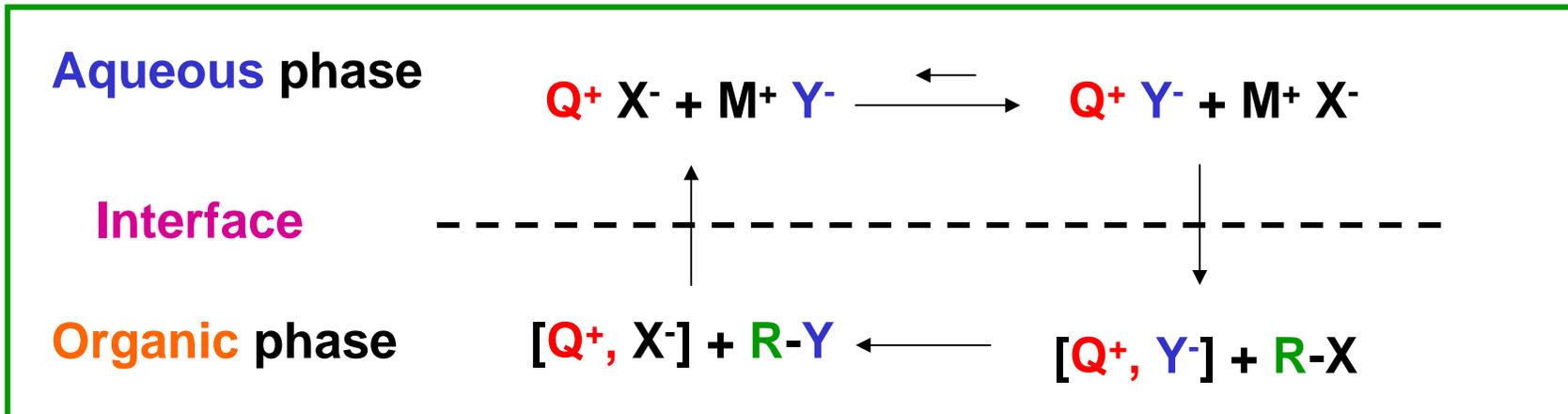
#### 4) Phase-transfer catalysis (PTC)

Aqueous phase and organic phase

Catalyst: quaternary ammonium salt

Function by transporting a nucleophilic monomer from the aqueous phase to organic phase, where its nucleophilicity is greatly enhanced because of reduced solvation effects





$Q^+ = \text{R}_4\text{N}^+, \text{R}_4\text{P}^+$  **Quarternary onium salt** selected due to its **high solubility** in the organic phase

$Q^+$  transfers anion  $Y^-$  into the **organic phase** as  $[Q^+, Y^-]$ , which then react with an alkyl halide  $\text{RX}$  to give the substitution product  $\text{R-Y}$

The produced  $Q^+X^-$  is rapidly reconverted into  $Q^+Y^-$  by **anion exchange** with **nucleophile**  $M^+Y^-$  from the aqueous phase.

## 10.8 Dendritic Polymers

- Potential **applications**: **drug delivery** systems, **controlled release** of agricultural chemicals, **molecular sensors**, **rheology modifiers**
- **Characteristic features** of dendrimers
  1. Three component parts: a central **core**, an **interior dendritic structure**, and an **exterior surface**
  2. Macromolecular **dimensions** are easily controlled by a **repetitive sequence** of synthetic steps.
  3. **More soluble** than linear polymers
    - ∴ **High surface functionality**
  4. **Lack** of **chain entanglement** → **Low viscosity**
  5. Supramolecular assemblies by incorporating **guest molecules** among the **interior branches** of the dendrimer.

- **Two approaches** to construct dendrimers

1. **Divergent** synthesis

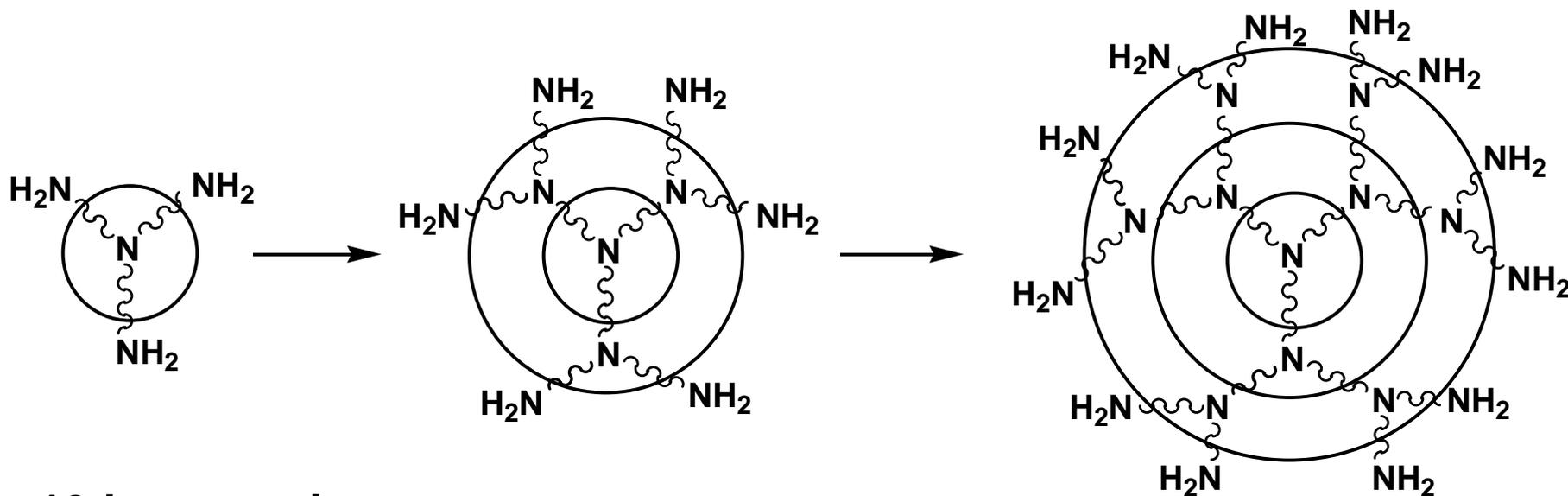
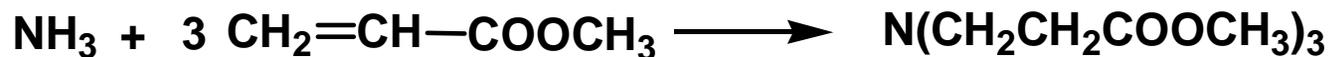
Branch points are constructed in a stepwise fashion **from a central core.**

2. **Convergent** synthesis

**Branch segments** are **constructed separately** and then joined to a **multifunctional core.**

## Divergent synthesis

### Polyamidoamine (PAMAM) dendrimers

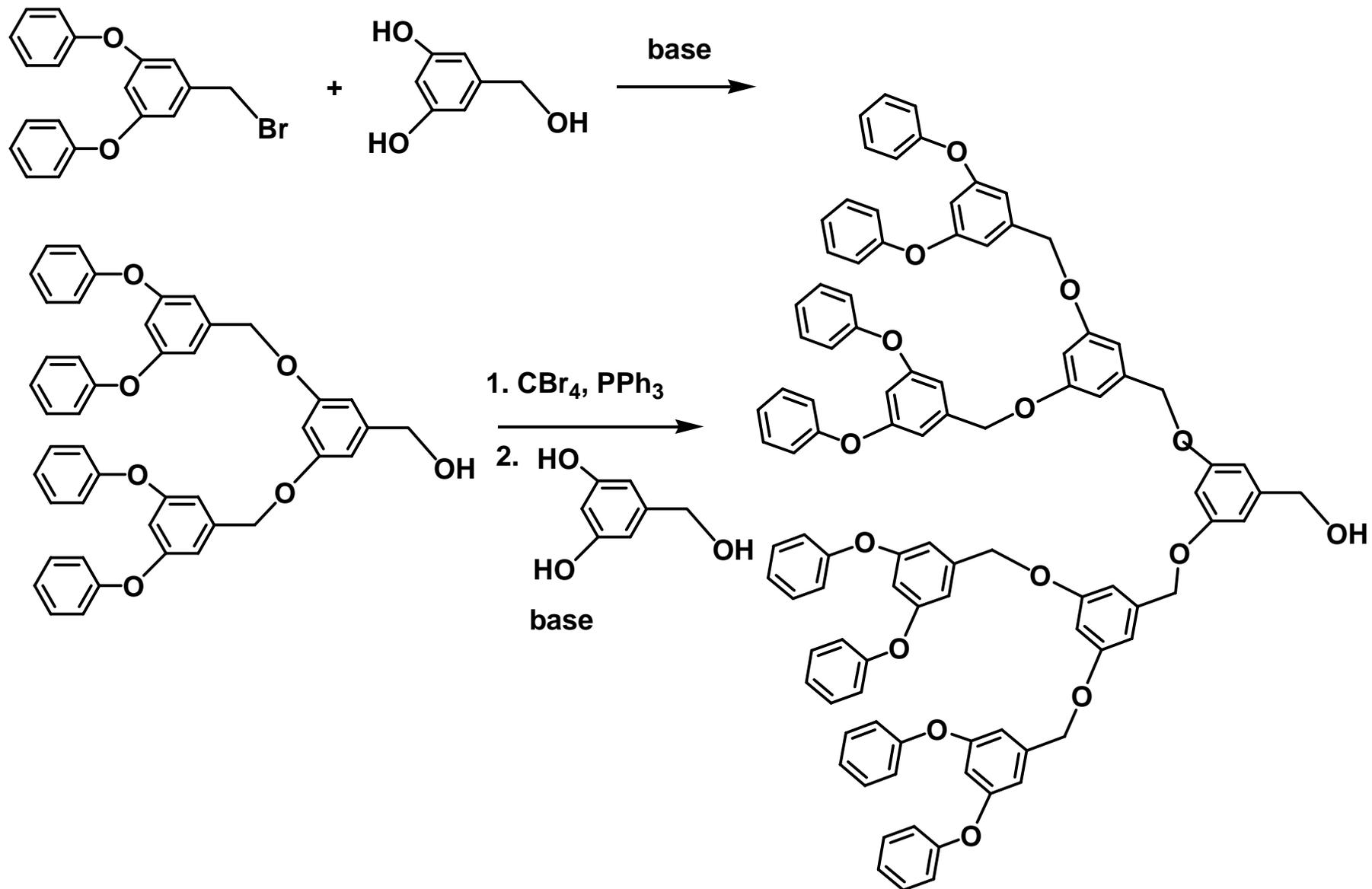


10th generation

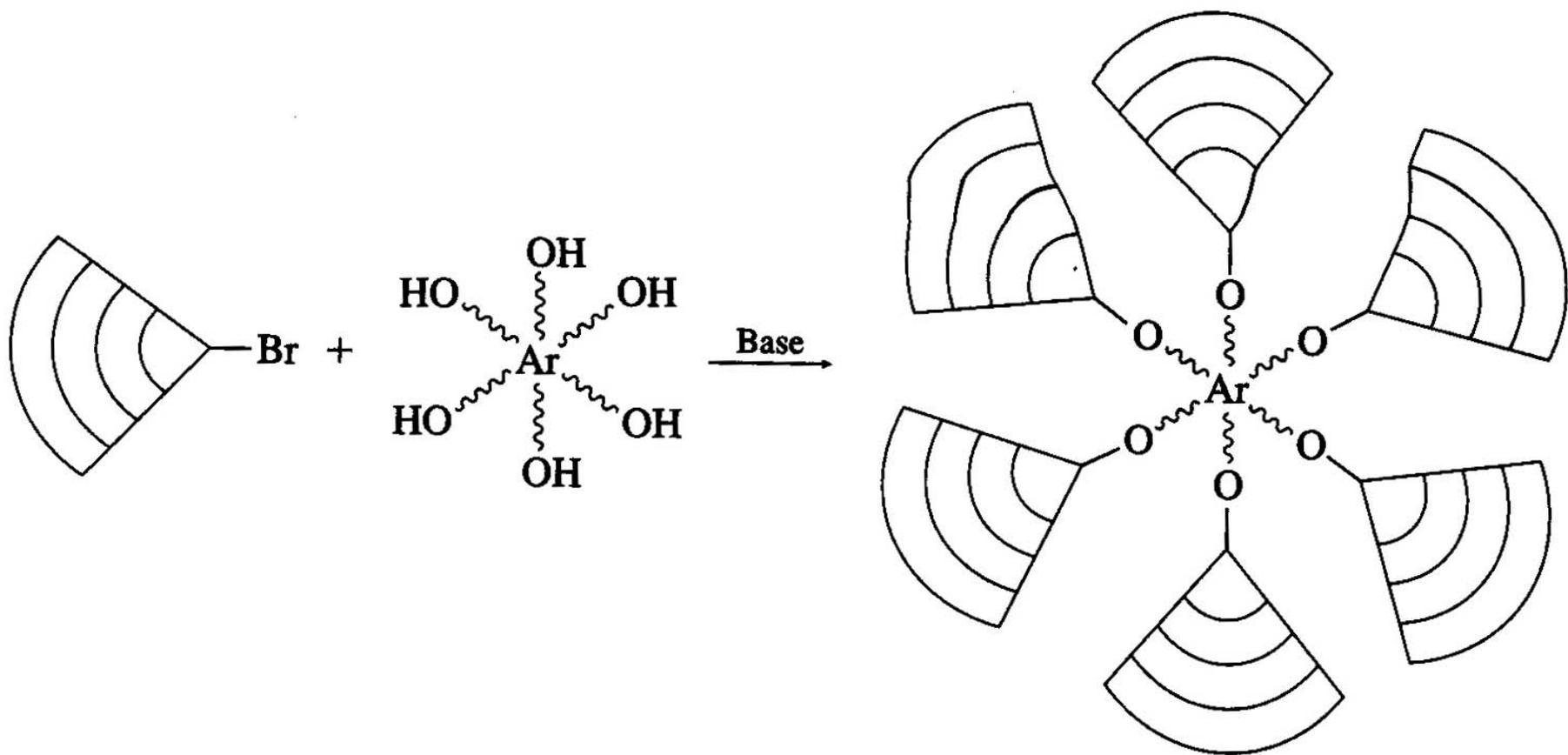
# of surface functional groups =  $3 \times 2^{10} = 3072$

Surface area: 100 times

## Convergent synthesis



### Scheme 10.3 Convergent synthesis of a dendrimer from dendritic segments.



## Hyperbranched polymers

More **random architectures** and do **not** emanate **from a central core**.

Synthesized from **AB<sub>x</sub>** functional monomers

Polymerization occurs via **dendritic branching** with **no** possibility of **crosslinking**

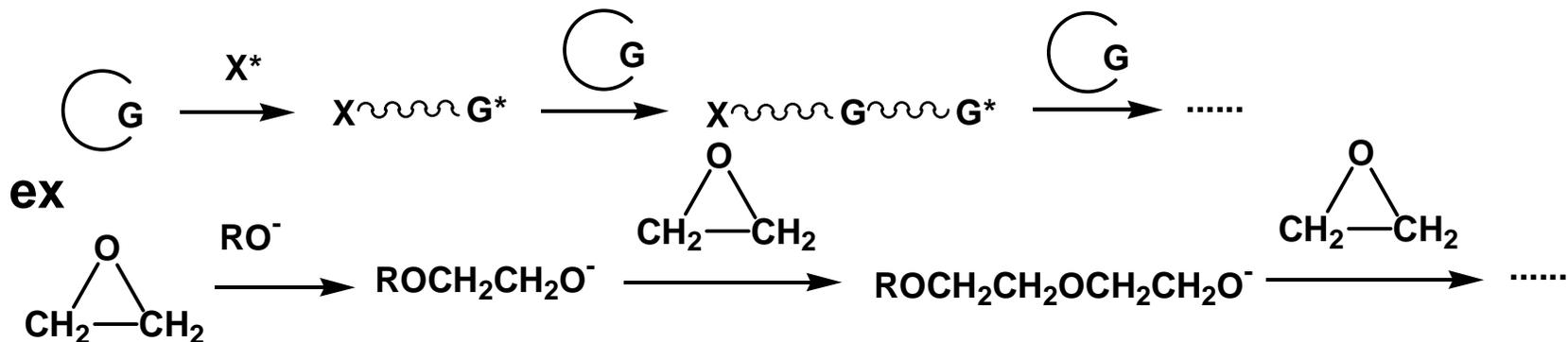


# 10.9 Ring-Opening Polymerization

## • Mechanisms

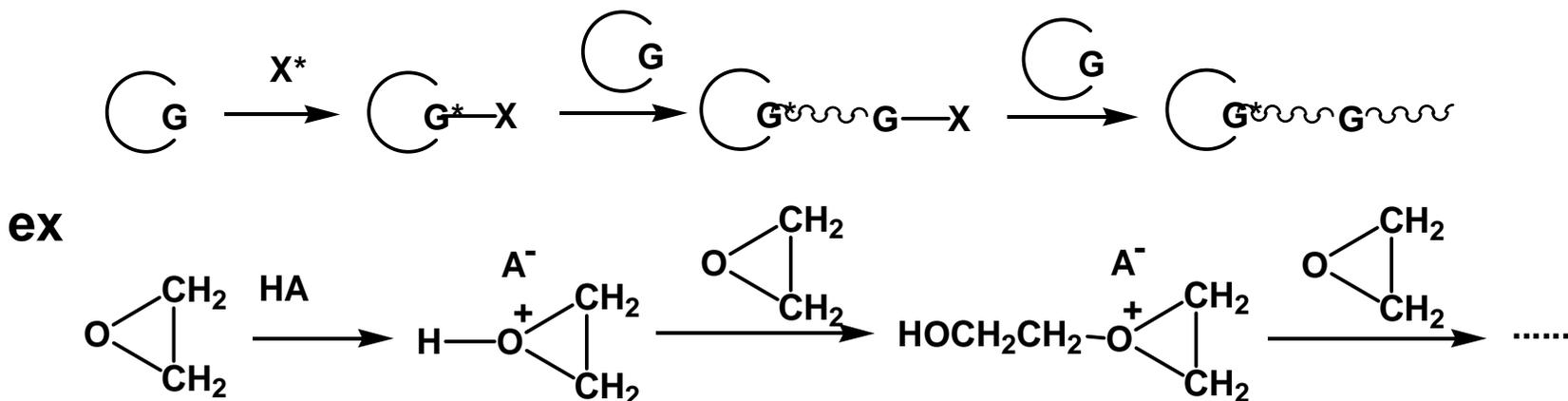
1. Monomer is attacked by **ionic or coordination species ( $X^*$ )**

→ Ring opening



2. Monomer is attacked by  $X^*$  → **Coordination species**

→ Second monomer → Ring opening



## Reactivity from ring strain



6-membered cyclic esters (lactones)  $\longrightarrow$  polyesters

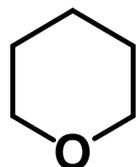
6-membered cyclic amides (lactams)  $\not\rightarrow$  polyamides

5-membered cyclic esters (lactones)  $\not\rightarrow$  polyesters

5-membered cyclic amides (lactams)  $\longrightarrow$  polyamides

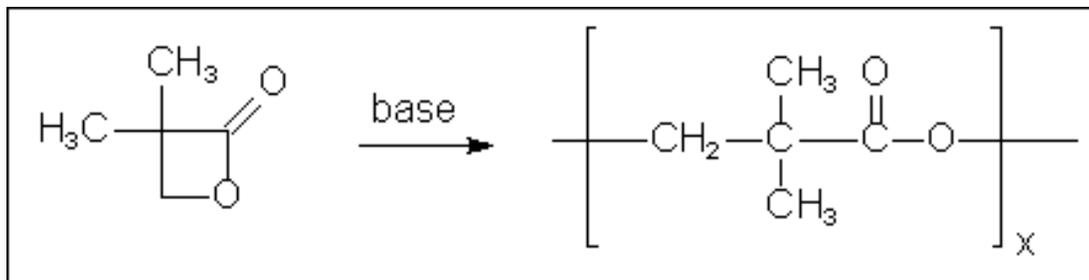
## Cyclic ethers

### Reactivity

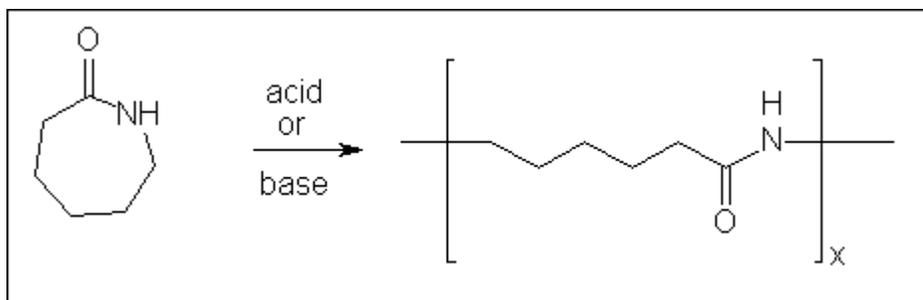


$\not\rightarrow$  polyether

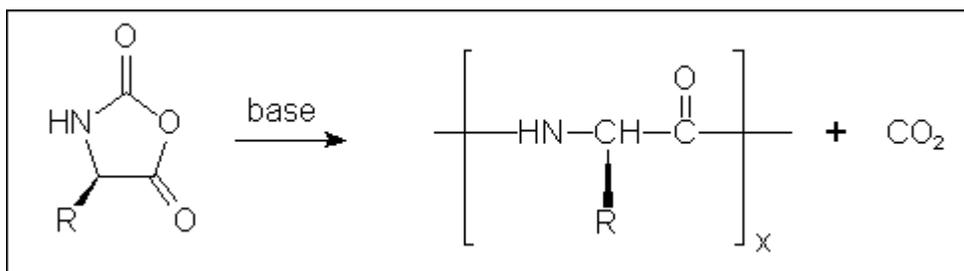
## Polyesters



## Polyamides

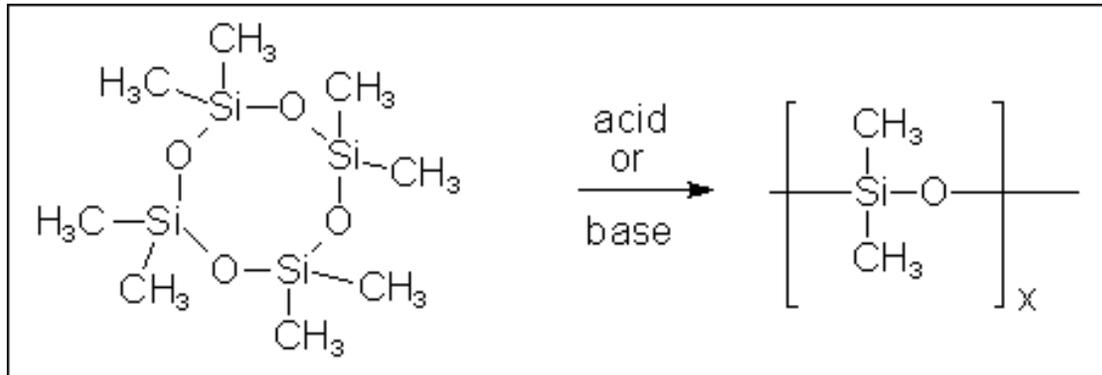


## Ring-Opening Polymerization of N-Carboxy Anhydrides



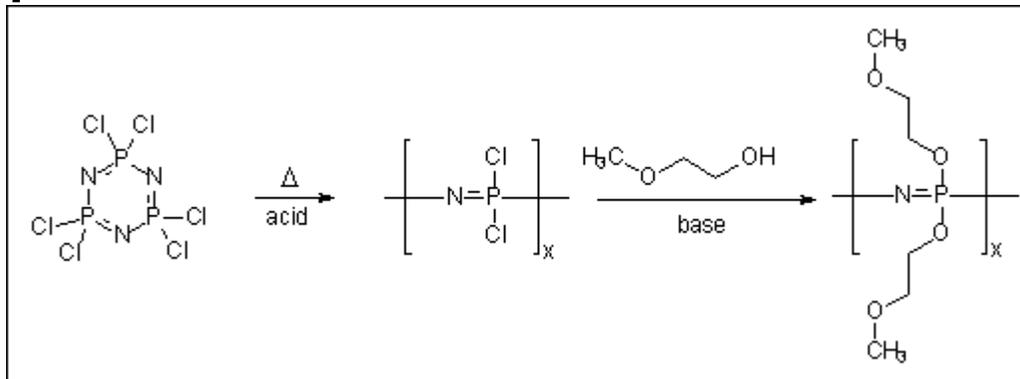
The product polymer is a **poly(amino acid)** or **polypeptide** or **synthetic protein**. This particular reaction is noteworthy because it is a chain reaction that occurs with expulsion of a small molecule ( $\text{CO}_2$ ). Such reactions are very rare.

## Silicones



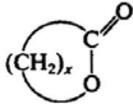
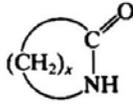
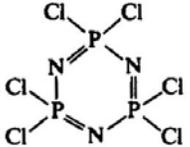
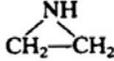
An example of an polymer with an **inorganic backbone** that can also be made by step polymerization.

## Polyphosphazenes



An example of a completely **inorganic polymer** that can be **functionalized** with organic groups after polymerization.

**TABLE 10.2.** Commercially Important Polymers Prepared by Ring-Opening Polymerization

| <i>Polymer Type</i>    | <i>Polymer Repeating Group</i>                                                                       | <i>Monomer Structure</i>                                                             | <i>Monomer Type</i>                         | <i>Chapter</i> |
|------------------------|------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------|----------------|
| Polyalkene             | $-\{\text{CH}=\text{CH}(\text{CH}_2)_x\}-$                                                           |    | Cycloalkene                                 | 8              |
| Polyether              | $-\{\text{CH}_2\text{O}\}-$                                                                          |    | Trioxane                                    | 11             |
| Polyether              | $-\{(\text{CH}_2)_x\text{O}\}-$                                                                      |    | Cyclic ether <sup>a</sup>                   | 11             |
| Polyester <sup>b</sup> | $-\left[ (\text{CH}_2)_x \text{CO} \right]-$                                                         |    | Lactone                                     | 12             |
| Polyamide              | $-\left[ (\text{CH}_2)_x \text{CNH} \right]-$                                                        |    | Lactam                                      | 13             |
| Polysiloxane           | $\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{SiO} \\   \\ \text{CH}_3 \end{array} \right]-$    |    | Cyclic siloxane                             | 16             |
| Polyphosphazene        | $\left[ \begin{array}{c} \text{Cl} \\   \\ \text{P}=\text{N} \\   \\ \text{Cl} \end{array} \right]-$ |   | Hexachloro-cyclotriphosphazene <sup>c</sup> | 16             |
| Polyamine              | $-\{\text{CH}_2\text{CH}_2\text{NH}\}-$                                                              |  | Aziridine <sup>d</sup>                      | 17             |

<sup>a</sup>Epoxide ( $x = 2$ ); oxetane ( $x = 3$ ).

<sup>b</sup>Ring opening of cyclic oligomers has also been developed.

<sup>c</sup>Phosphonitrilic chloride trimer.

<sup>d</sup>Also called alkyleneimine.