Polymerisation Reactions

Distinguishing features of Chain- and Step-Polymerisation mechanisms:

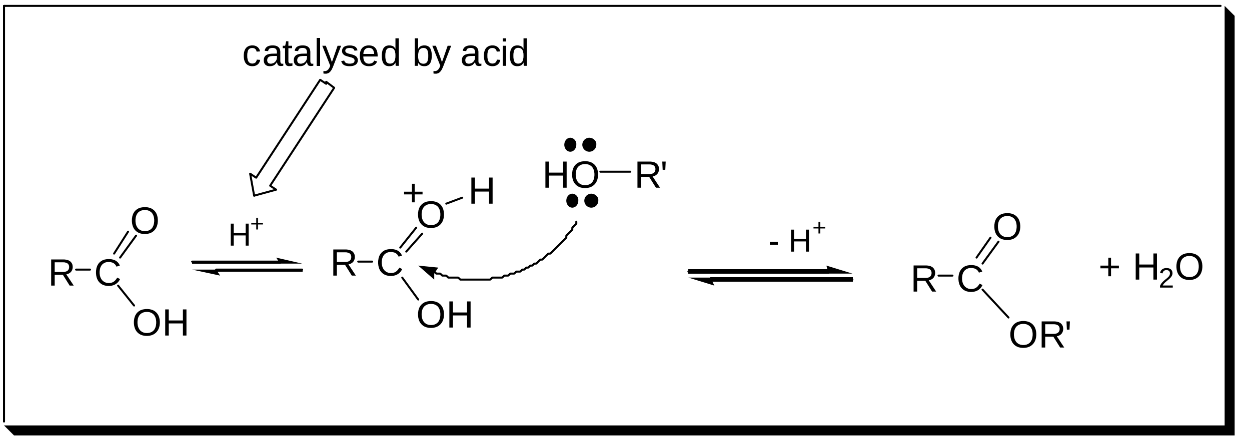
Chain polymerisations **(Vinyl monomers)**	**Stepwise polymerisation =** ***"polycondensation"***
Reactive chain end adds monomer units one at a time	Any two molecular species can react
Monomer concentration decreases steadily throughout reaction	Monomer disappears early in the reaction: *at DP = 10 less than 1% monomer remains*
High-molecular weight polymer is formed at once, MW changes little throughout reaction	Polymer MW rises steadily, rapid increase only in last stages of reaction
Long reaction times increase yields but not molecular weight	Long reaction times essential for high mol. weight
Reaction mixture contains only monomer, high-MW polymer, 10^{-8} parts of growing chains	At any stage monomer, oligomers, polymers present. All molecular species contribute to growth.

Step Polymerisation Reactions

Condensation reactions of di-carboxylic acids: most important reaction for the preparation of polymers by stepwise reactions.

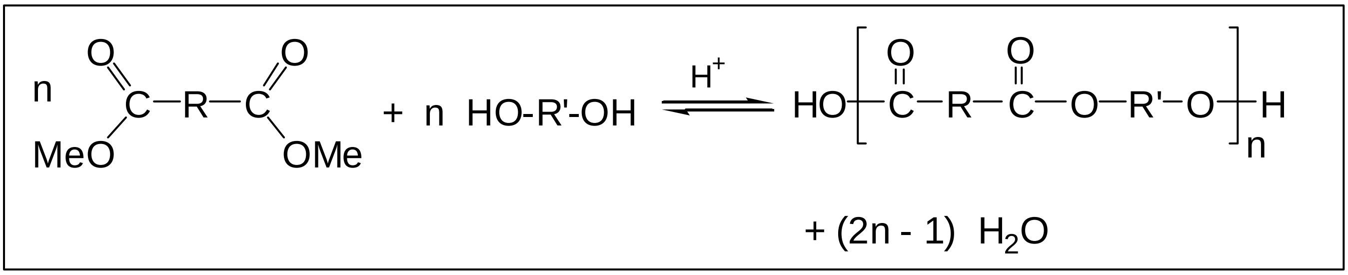
Polyesters

Alcohol + acid: Esterification



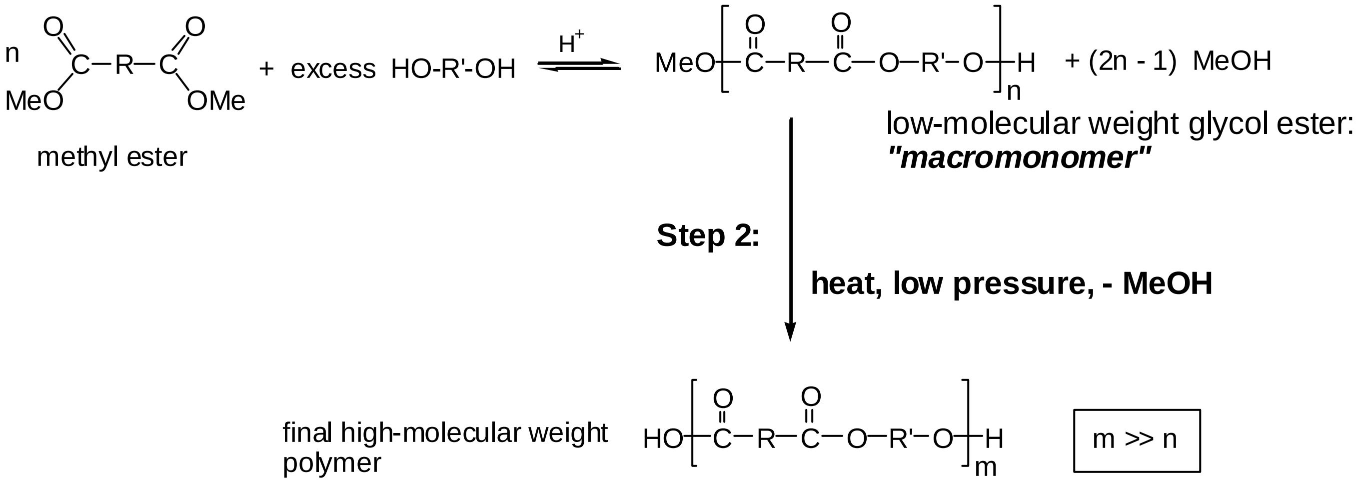
The reaction is an equilibrium. In order to get good yields, the water must be removed.

Using di-basic acids and diols gives polymers:

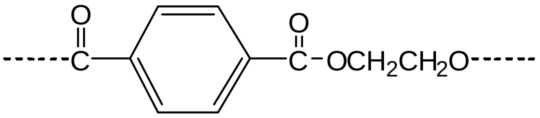


In practice, the equilibrium is not very favourable and water is difficult to remove. Polyesters are therefore made in a two-step process:

Step 1:



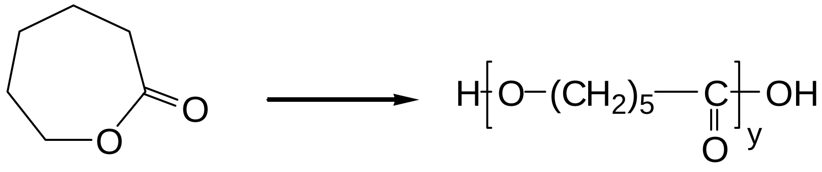
Linear aliphatic polyesters have low melting points and high solubility and are not useful. Stiffer building blocks give high-melting polymers:



poly(ethylene terephthalate)

for films, plastic drinks bottles, etc.

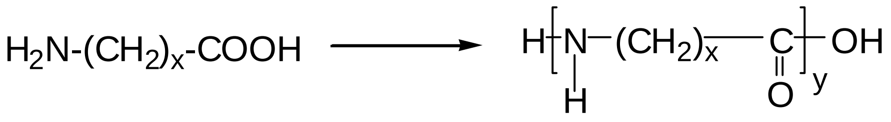
Homopolymerisation of cyclic esters is also practised:



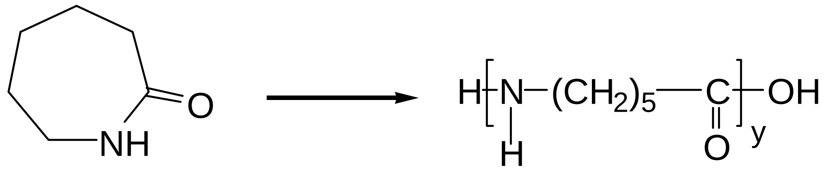
carpolactone

Polyamides

Homopolymerisation of ω-aminoacids:



$$H_2N\text{-}(CH_2)_x\text{-}COOH \longrightarrow H\left[\underset{\underset{H}{|}}{N}-(CH_2)_x-\underset{\underset{O}{\|}}{C}\right]_y OH$$

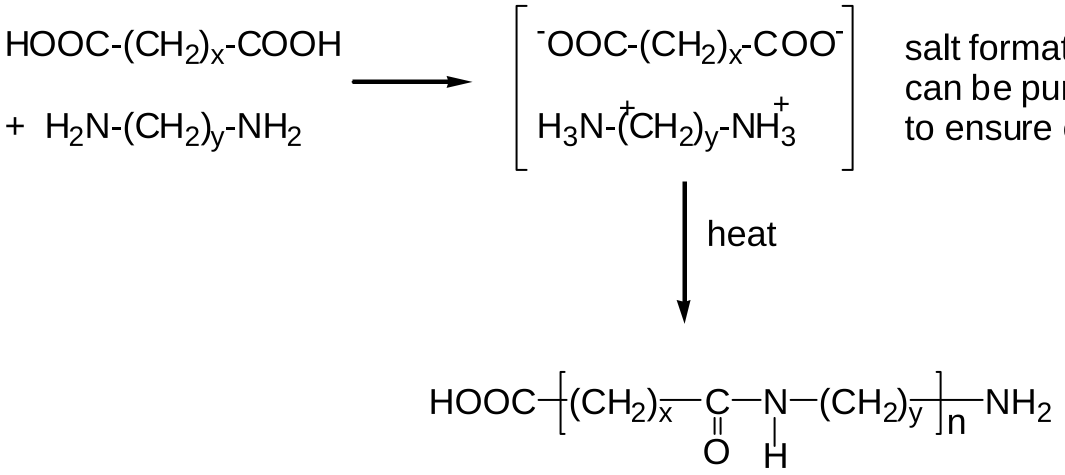


$$\longrightarrow H\left[\underset{\underset{H}{|}}{N}-(CH_2)_5-\underset{\underset{O}{\|}}{C}\right]_y OH$$

caprolactam

Nylon-6

Condensation of diacids with diamines:



$$\begin{array}{l} HOOC\text{-}(CH_2)_x\text{-}COOH \\ +\ H_2N\text{-}(CH_2)_y\text{-}NH_2 \end{array} \longrightarrow \left[\begin{array}{c} {}^{-}OOC\text{-}(CH_2)_x\text{-}COO^{-} \\ H_3\overset{+}{N}\text{-}(CH_2)_y\text{-}\overset{+}{N}H_3 \end{array}\right]$$

$$\Big\downarrow \text{heat}$$

$$HOOC\left[(CH_2)_x-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-(CH_2)_y\right]_n NH_2$$

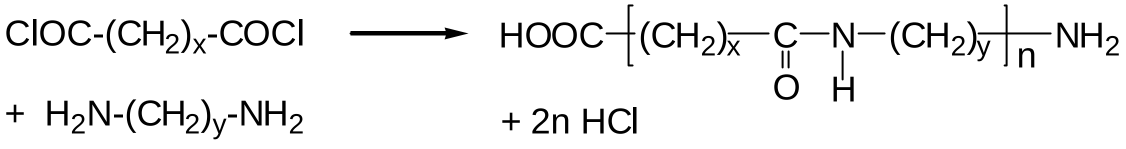
salt formation
can be purified by crystallisatio
to ensure exact stoichiometry

If x = 4 and y = 6 ➔ **Nylon-66**

launched nylon production from 1935

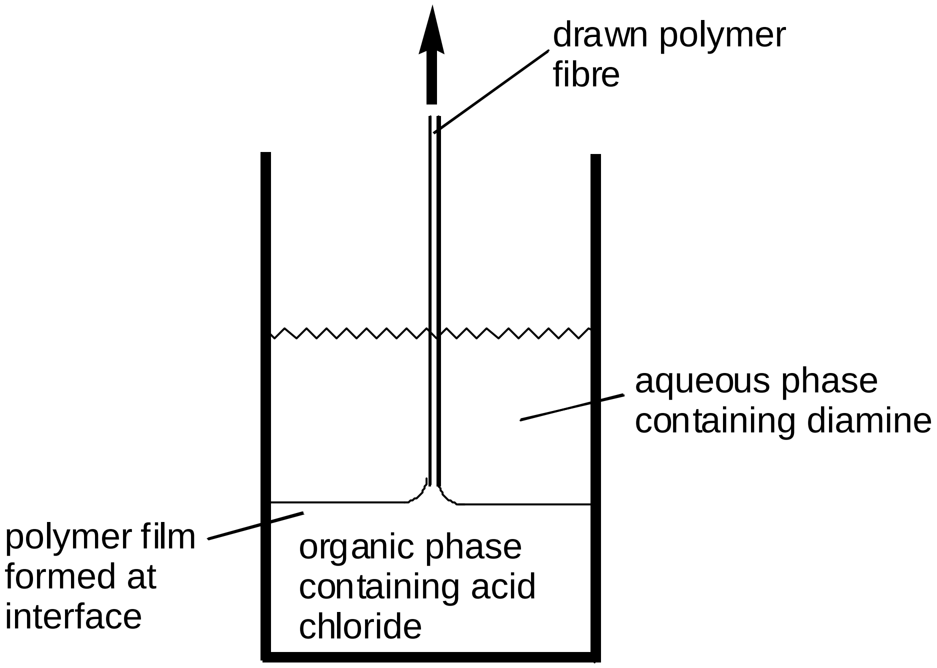
high melting (mp. 265°C), pliable, silk-like fibre

Condensation of acid chlorides with diamines:



$$\begin{array}{l} ClOC\text{-}(CH_2)_x\text{-}COCl \\ +\ H_2N\text{-}(CH_2)_y\text{-}NH_2 \end{array} \longrightarrow \begin{array}{l} HOOC\left[(CH_2)_x-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-(CH_2)_y\right]_n NH_2 \\ +\ 2n\ HCl \end{array}$$

Acid chlorides are much more reactive. Polymers can be made at room temperature: Interfacial condensation:



Natural polyamides:

- Polypeptides
- Wool
- Silk

Kinetics of Step Reactions

In a polyester formation, the disappearance of –COOH groups can be described by the equation:

$$\frac{-\,d\,[\mathrm{COOH}]}{dt} = k\,[\mathrm{COOH}][\mathrm{OH}]$$

Definitions:

c_0 = initial concentration of functional groups,

c = concentration at any given time,

p = progress of the reaction,defined as fraction of functional groups that has reacted at time t. It follows;

$$c = c_0(1 - p)$$

With bifunctional reactants, if N_0 = initial number of functional groups,

N = number of functional groups at time t, then the number-average degree of polymerisation DP_n is given by:

$$\boxed{DP_n = \frac{N_0}{N} = \frac{c_0}{c} = \frac{1}{1 - p}}$$

“Carother’s equation”

Since all monomers can grow at the same time, the reaction gives oligomers unless very high conversions are achieved.

p	DP_n
0.90	10
0.95	20
0.99	100
0.999	1000

Since [COOH] = [OH], the rate equation becomes:

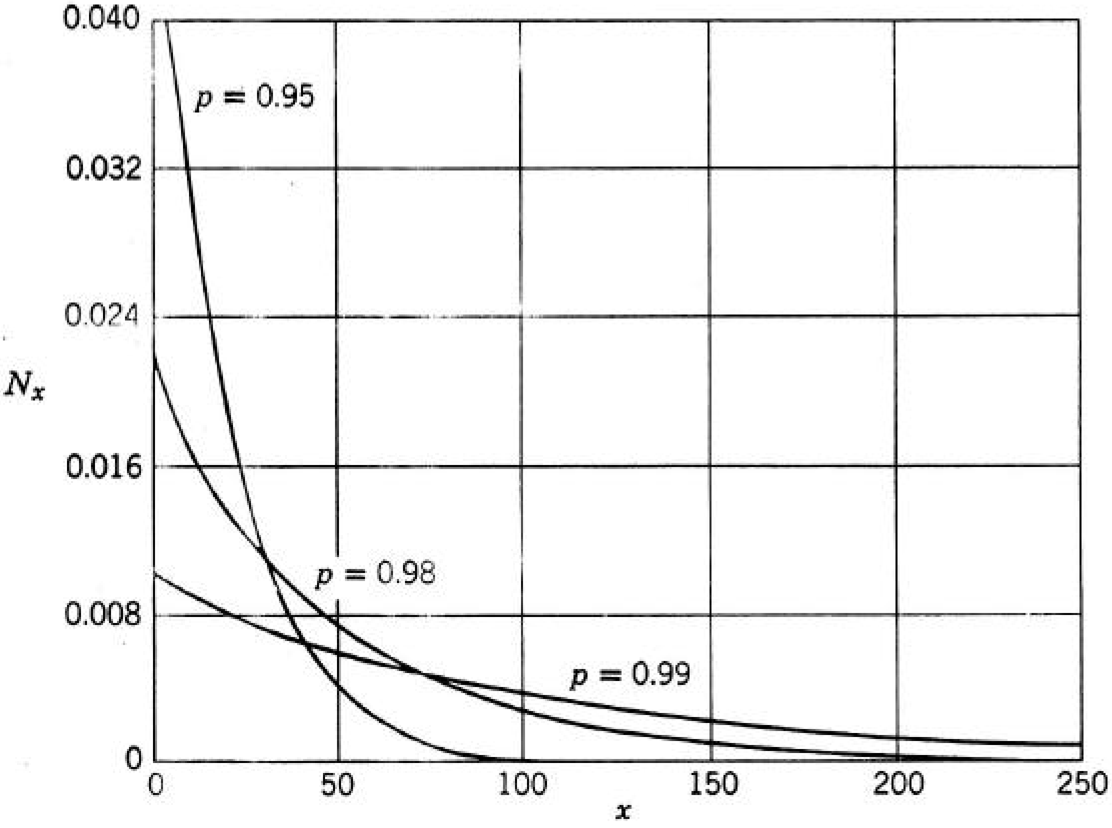
$$-dc/dt = kc^2$$

Integration:

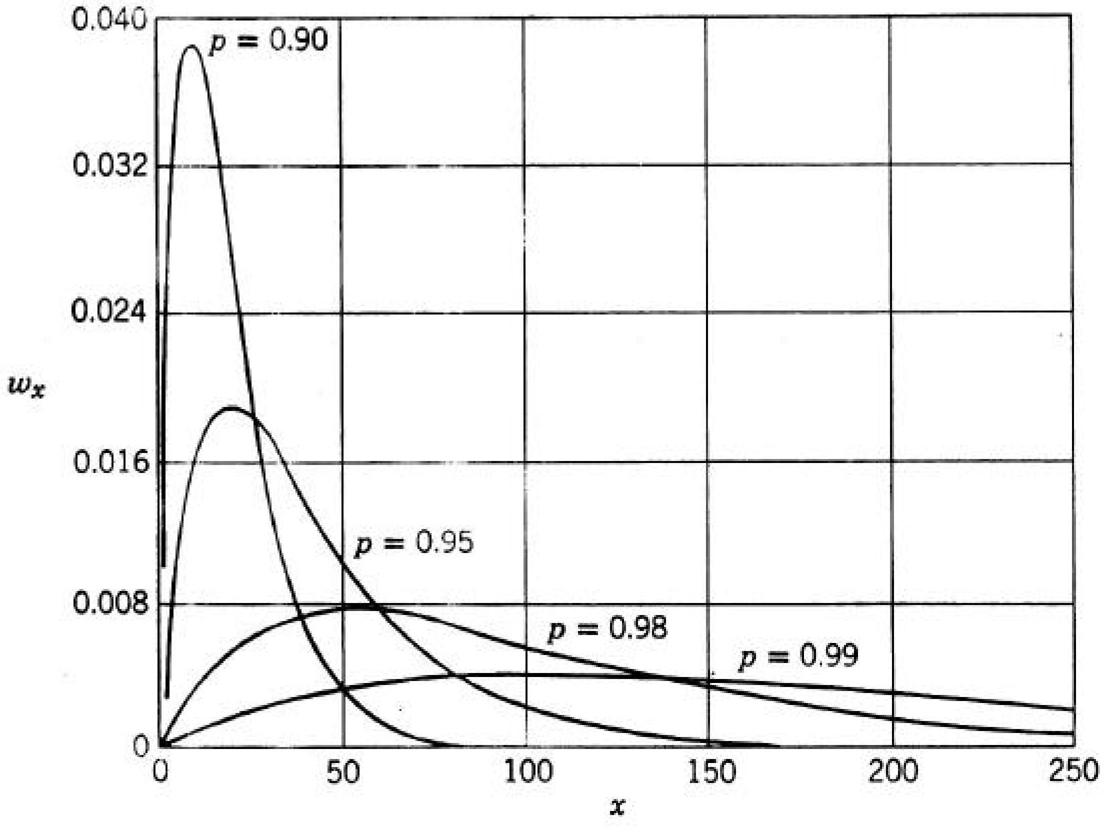
$$c_0kt = \frac{1}{1 - p} + \text{const.}$$

➔ DP_n increases linearly with reaction time

Mol-fraction distribution of chain molecules in a linear step-reaction polymer for several extents of reaction p:



Weight fraction distribution:

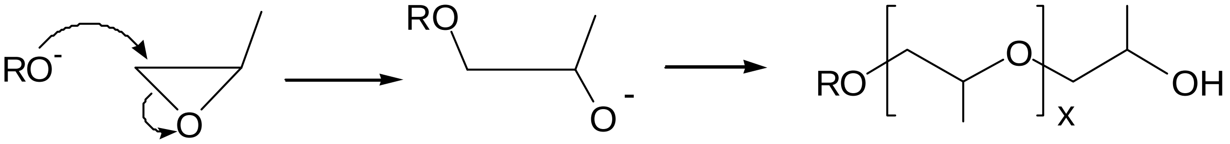


➔ In a step-polymerisation, where the polymerisation is an equilibrium reaction, the reaction needs to go to very high convertion (>> 99.9%) to achieve a high molecular weight.

Since step reactions are equilibria, a large polymer chain is subject to attack and "back-biting" ➔ ring formation
Needs to be avoided by control of stoichiometry and reaction conditions, e.g. avoid exposure to catalyst once monomers have been consumed.

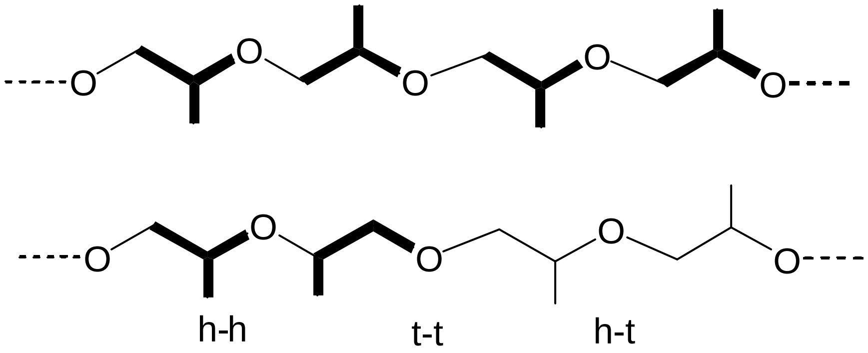
Other step polymerisations:

Epoxide polymerisation



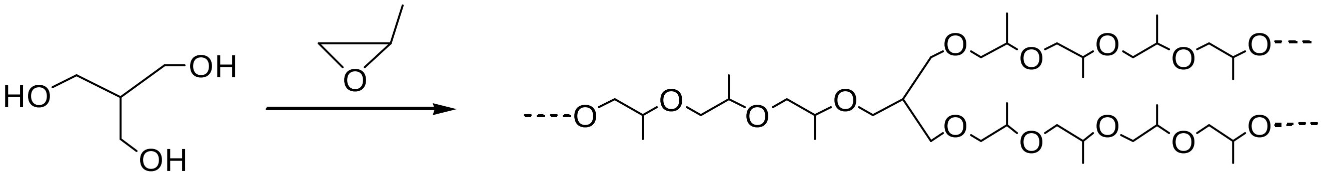
Large scale polymerisation of propylene oxide.

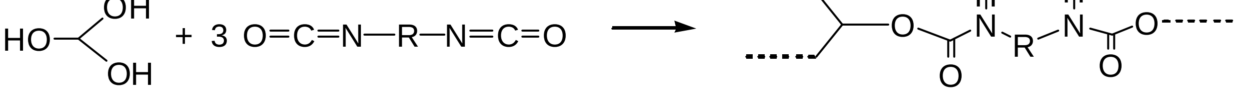
Regioisomers:



Epoxides are also polymerised cationically and by a coordination mechanism.

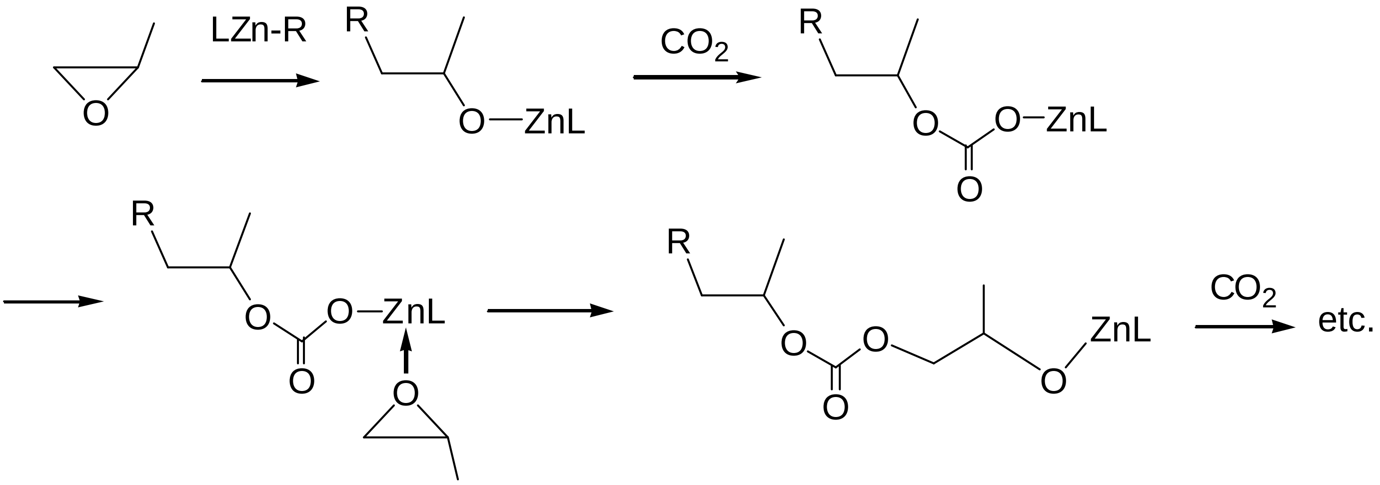
With tri-functional alcohols, branched products are produced polyurethane products



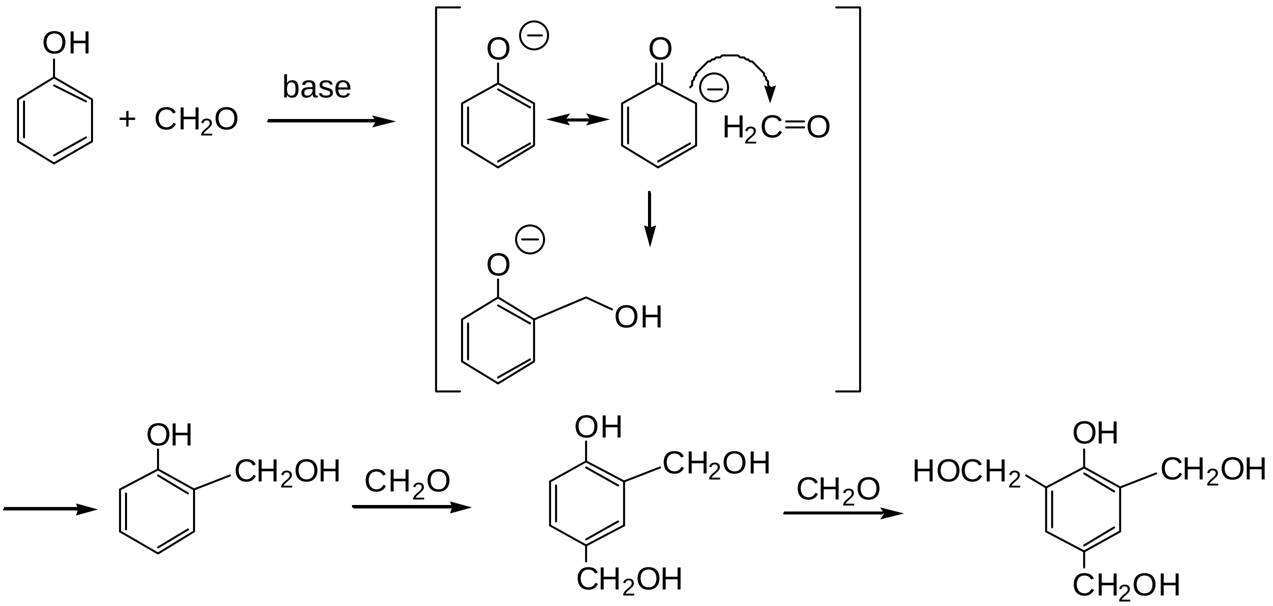


branched polyurethane

Epoxide / CO_2 copolymerisation to polycarbonates:



Phenol-Formaldehyde Resins:



Further condensation catalysed by acids or bases gives methylene-bridged networks: ➔thermosets