Polymer Chemistry

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Polymer Science and Technology

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2. Condensation Polymerization

I. Polymerization mechanism

1. Polymers are classified as **addition** or **condensation** polymers depending on the **type of polymerization** reaction involved in their synthesis.

2. Classification of polymerization processes into three classes: **condensation**, **addition**, and **ring-opening** polymers, is based on the **structures of the starting monomers**.

3. Most general classification scheme is based on the **polymer synthesis**: **step-reaction** (condensation) or **chain-reaction** (addition) polymerization.

TABLE 2.3 *Distinguishing Features of Chain and Step Polymerization Mechanisms*

Chain Polymerization	Step Polymerization
Only growth reaction adds repeating unit one at a time of the chain.	Any two molecular species present can react.
Monomer concentration decreases steadily throughout reaction.	Monomer disappears early in reaction: at DP 10, less than 1% monomer remains.
High polymer is formed at once; polymer molecular weight changes little throughout reaction.	Polymer molecular weight rises steadily throughout reaction.
Reaction mixture contains only monomer, high polymer, and about 10^{-5} part of growing chains.	At any stage all molecular species are present in a calculable distribution.

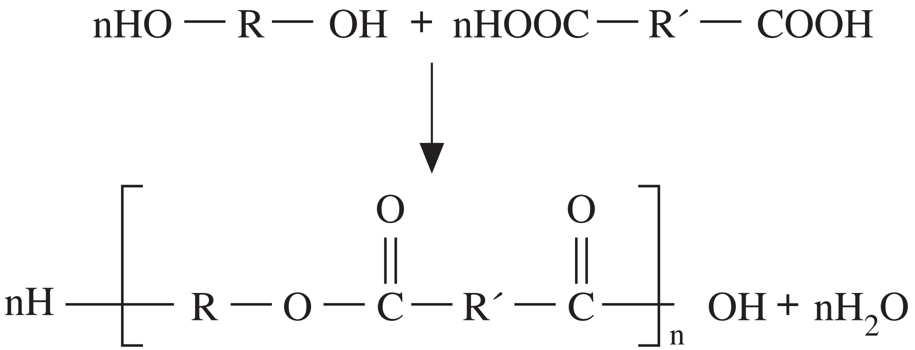
III. CONDENSATION (STEP-GROWTH) POLYMERIZATION

Step-growth polymerization involves a series of reactions in which any two species (monomers, dimers, trimers, etc.) can react at any time, leading to a larger molecule.

Most step-growth polymerizations involve a classical condensation reaction such as esterification, ester interchange, or amidization.

In step-growth polymerization, the stepwise reaction occurs between pairs of chemically reactive or functional groups on the reacting molecules.

In most cases, step-growth polymerization is accompanied by the elimination of a small molecule such as water as a by-product.

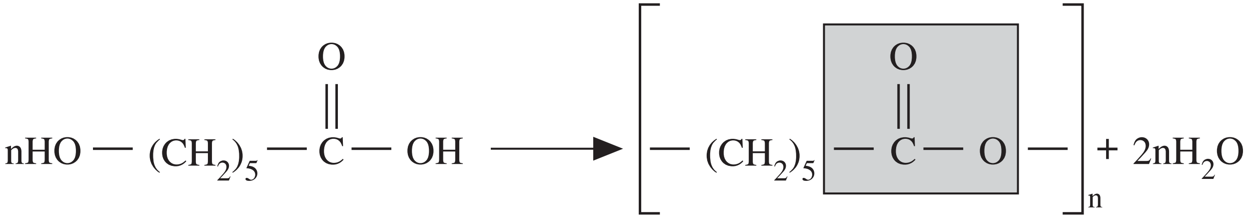


$$nHO-R-OH + nHOOC-R'-COOH \longrightarrow nH\left[-R-O-\overset{\overset{\displaystyle O}{\|}}{C}-R'-\overset{\overset{\displaystyle O}{\|}}{C}-\right]_n OH + nH_2O$$

Step-growth polymerizations generally involve either one or more types of monomers. In either case, each monomer has at least two reactive (functional) groups.

In cases where only one type of monomer is involved, which is known as A-B step-growth polymerization, the functional groups on the monomer are different and capable of intramolecular reactions.

An example is the formation of an aliphatic polyester by the self-condensation:



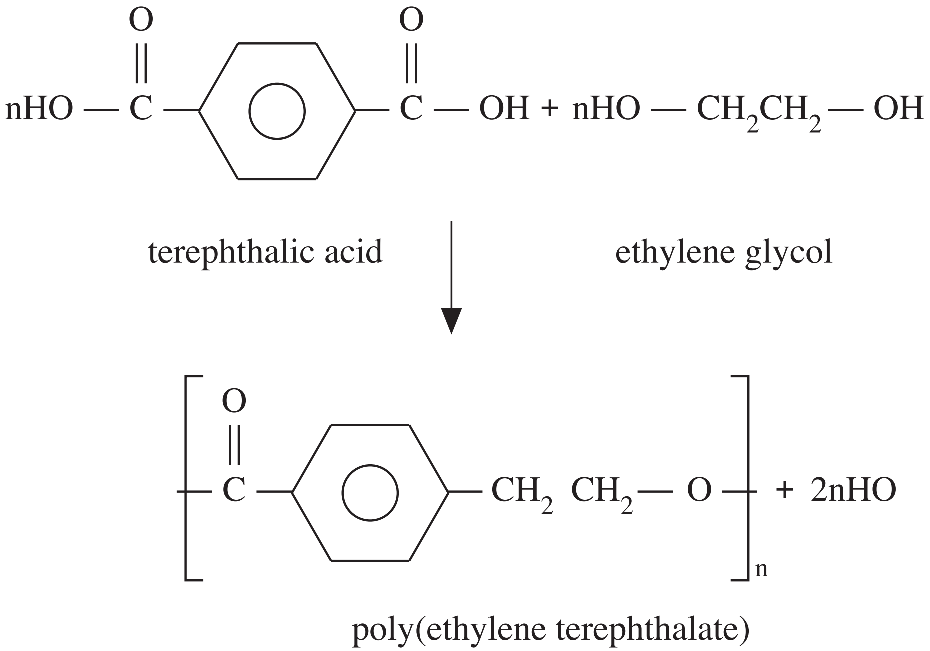
$$nHO-(CH_2)_5-\overset{\overset{O}{\|}}{C}-OH \longrightarrow \left[-(CH_2)_5-\boxed{\overset{\overset{O}{\|}}{C}-O}-\right]_n + 2nH_2O$$

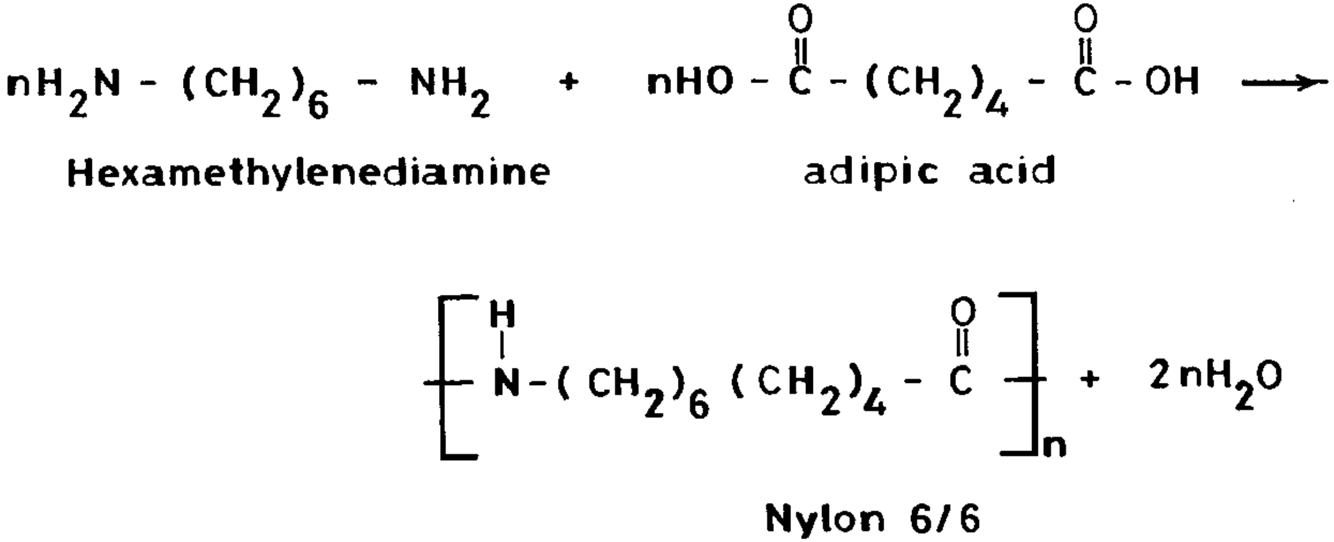
ω-hydroxycproic acid

polycaprolactone

In those cases where more than one type of molecule is involved, the functional groups on each type of monomer are the same, but capable of intermolecular reaction with the other type of monomer.

This is known as the A–A/B–B step-growth polymerization and is exemplified by the preparation of poly(ethylene terephthalate) and nylon 6,6:





$$nH_2N-(CH_2)_6-NH_2 + nHO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH \longrightarrow \left[-\overset{H}{\overset{|}{N}}-(CH_2)_6(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_n + 2nH_2O$$

Step-growth polymerizations can be divided into two main categories:

1. **polycondensation**, in which a small molecule is eliminated at each step,

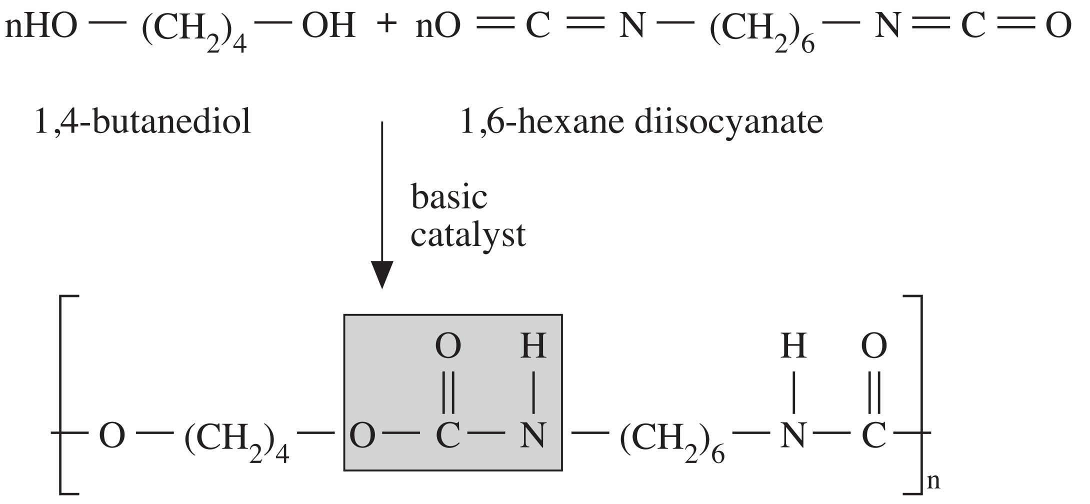
2. **polyaddition**, in which monomers react without the elimination of a small molecule.

$$A - R - A + B - R' - B \rightarrow A - R - R' - B + AB$$

polycondensation

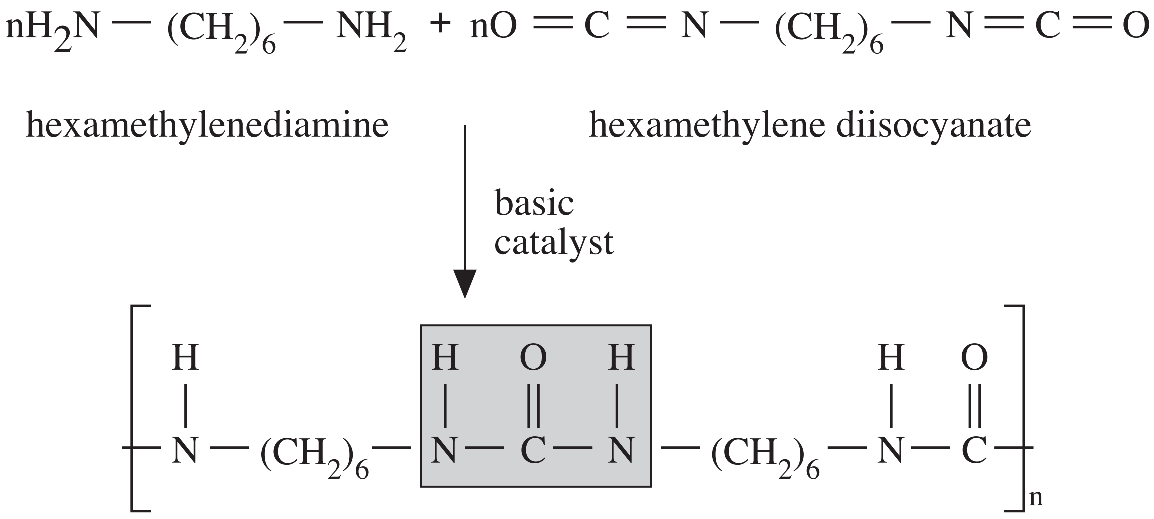
$$A - R - A + B - R' - B \rightarrow A - R - AB - R' - B$$

polyaddition



$$nHO-(CH_2)_4-OH + nO=C=N-(CH_2)_6-N=C=O \xrightarrow{\text{basic catalyst}} \left[-O-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}- \right]_n$$

polyurethane



$$nH_2N-(CH_2)_6-NH_2 + nO=C=N-(CH_2)_6-N=C=O \xrightarrow{\text{basic catalyst}} \left[-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}- \right]_n$$

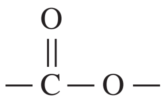
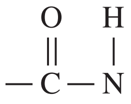
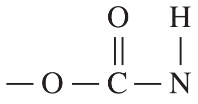
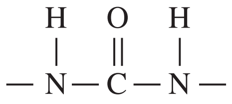
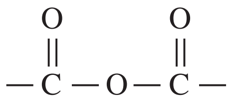
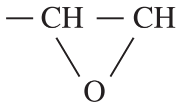
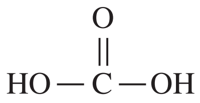
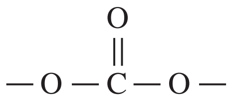
polyurea

In contrast to addition polymers, the structural unit in step-growth polymers is not identical chemically to the structure of the starting monomer(s).

Step-growth polymers derive their names from the reactive type (characteristic interunit linkage) involved in the polymerization.

For instance, in the reaction between the glycol and dicarboxylic acid, the resulting polymer is a polyester.

TABLE 2.2 *Some Functional Groups and Their Characteristic Interunit Linkage in Polymers*

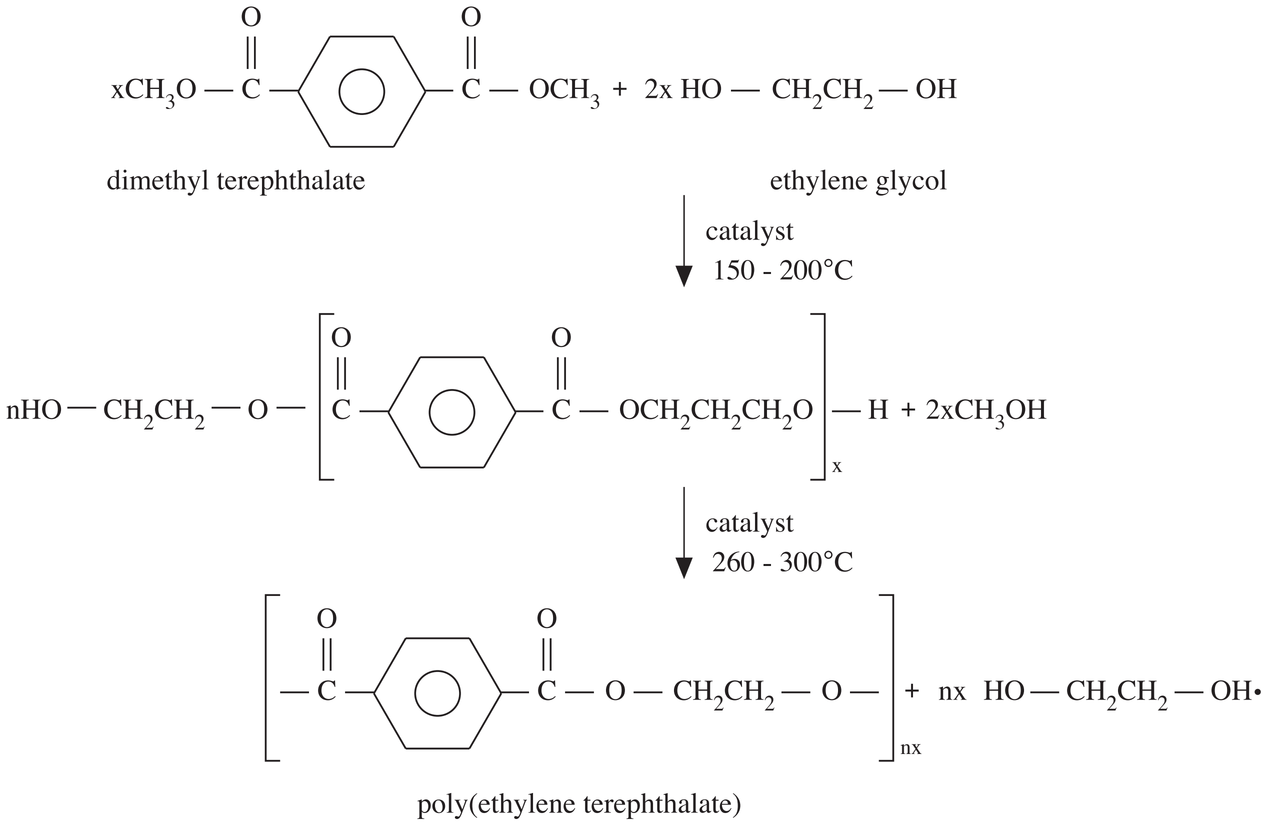
Reactants Functional Group	Characteristic Interunit Linkage	Polymer Type
$-OH + -COOH$	 $-\overset{O}{\overset{\Vert}{C}}-O-$	Polyester
$-NH_2 + -COOH$	 $-\overset{O}{\overset{\Vert}{C}}-\overset{H}{\overset{\vert}{N}}$	Polyamide
$-OH + -NCO$	 $-O-\overset{O}{\overset{\Vert}{C}}-\overset{H}{\overset{\vert}{N}}$	Polyurethane
$-NH_2 + -NCO$	 $-\overset{H}{\overset{\vert}{N}}-\overset{O}{\overset{\Vert}{C}}-\overset{H}{\overset{\vert}{N}}-$	Polyurea
$-COOH + -COOH$	 $-\overset{O}{\overset{\Vert}{C}}-O-\overset{O}{\overset{\Vert}{C}}-$	Polyanhydride
$-OH + -OH$	$-O-$	Polyether
	$-O-$	Polyether
 $HO-\overset{O}{\overset{\Vert}{C}}-OH$	 $-O-\overset{O}{\overset{\Vert}{C}}-O-$	Polycarbonate

A. TYPICAL STEP-GROWTH POLYMERIZATIONS

1. Polyesters

Poly(ethylene terephthalate) (PETP) is the largest volume synthetic fiber. It is also used as film (mylar) and in bottle applications.

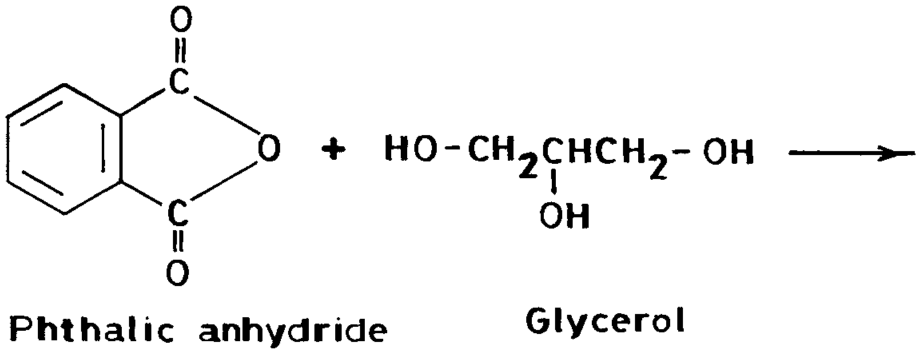
The traditional route for the production of commercial PETP is through two successive ester interchange reactions:



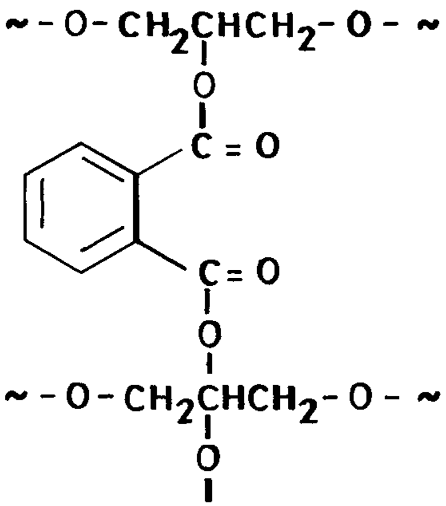
In the first step, a 1:2 molar ratio of dimethyl terephthalate to ethylene glycol is reacted in the presence of a catalyst such as calcium acetate, and an oligomeric product (x = 1 to 4) is obtained.

Poly(ethylene terephthalate) is a linear polyester obtained from the reaction of difunctional monomers. Branched or network polyesters are obtained if at least one of the reagents is tri- or multifunctional.

This can be achieved either by the use of polyols such as glycerol in the case of saturated polyesters (**glyptal**) or by the use of unsaturated dicarboxylic acids such as maleic anhydride in the case of unsaturated polyester.

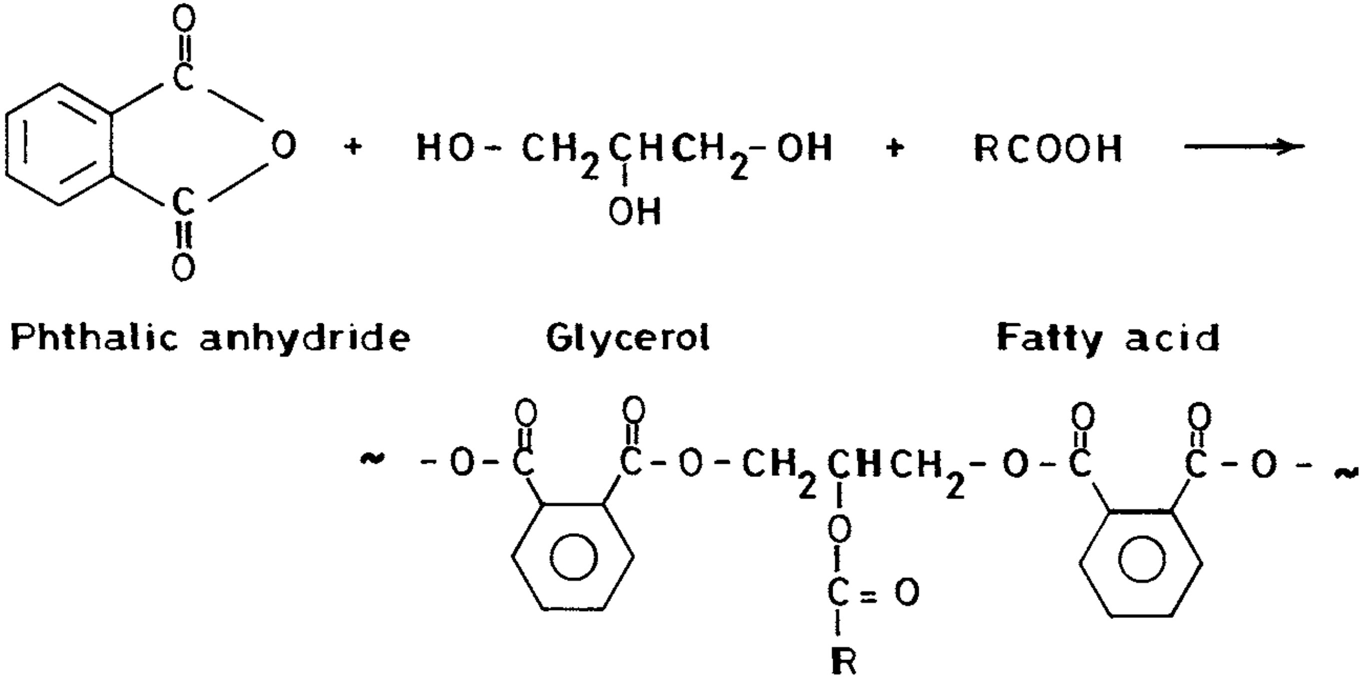


In the preparation of glyptal, glycerol and phthalic anhydride react to form a viscous liquid initially, which on further reaction hardens as a result of network formation.



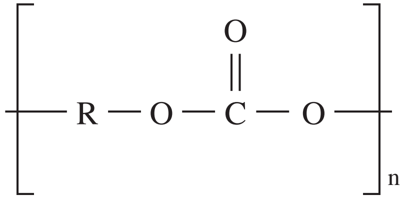
Glyptal is used mainly as an adhesive. Glyptal modified with natural or synthetic oils is known as an **alkyd resin**, which is a special polyester of great importance in the coatings industry.

The fatty acid RCOOH may be derived from vegetable drying oils (e.g., soybean, linseed oils) or from nondrying oils (e.g., coconut oil).



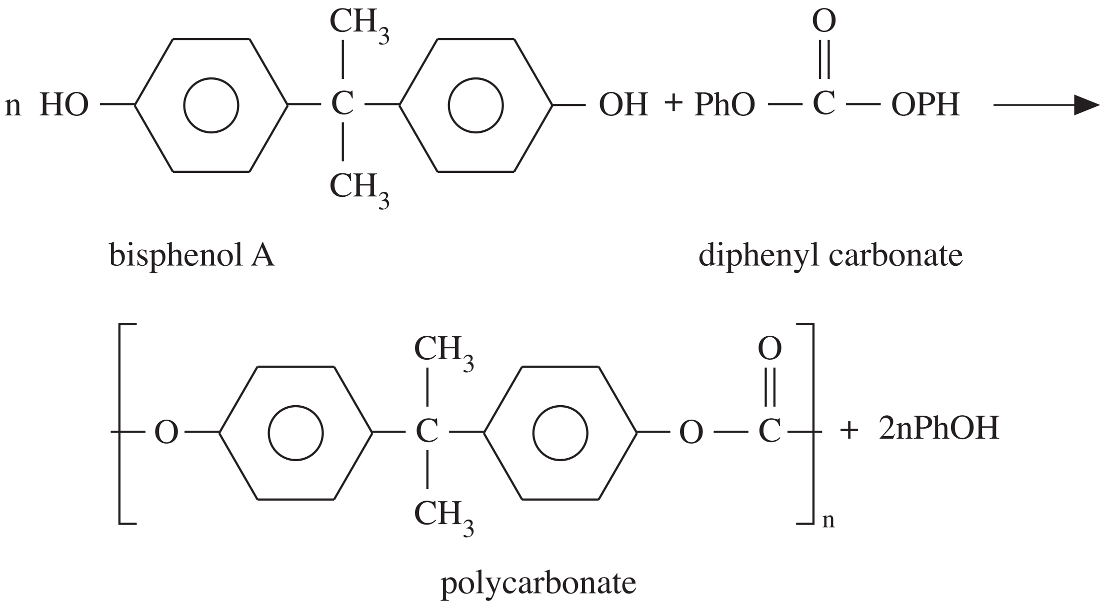
2. Polycarbonates

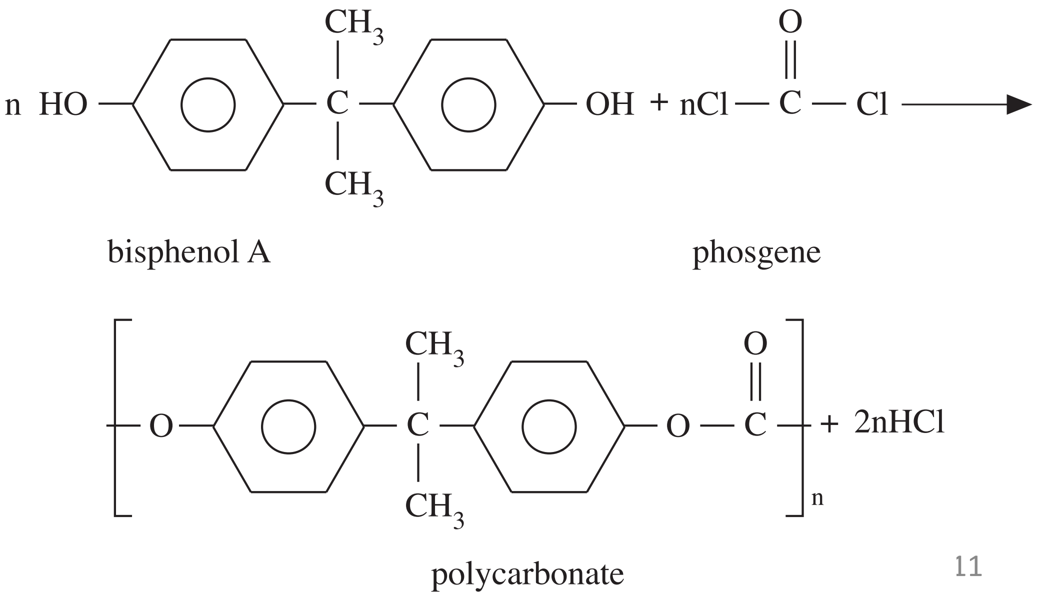
Polycarbonates are a special class of polyesters derived from carbonic acid (HO–CO–OH). Polycarbonates are the second largest by volume engineering thermoplastics next to polyamides.



$$\left[R - O - \overset{O}{\overset{\|}{C}} - O \right]_n$$

Their preparation involves the linking together of aromatic dihydroxy compounds, usually 2,2-bis(4-hydroxyphenyl) propane or bisphenol A, by reacting them with a derivative of carbonic acid such as phosgene or diphenyl carbonate.





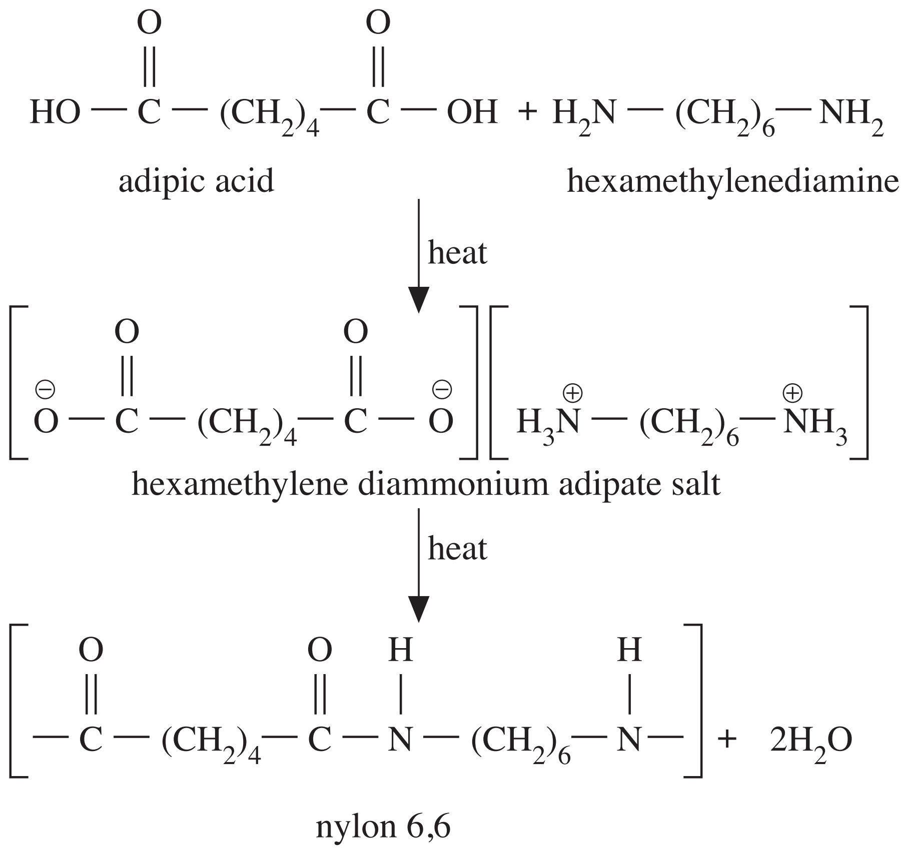
3. Polyamides

Polyamides, or nylons are characterized by the presence of amide linkages (–CONH–) on the polymer main chain.

There are **four synthetic routes**: (1) condensation reaction between a dicarboxylic acid and a diamine, (2) reaction between a diacid chloride and a diamine, (3) dehydration–condensation reactions of amino acids, and (4) ring-opening polymerization of lactams.

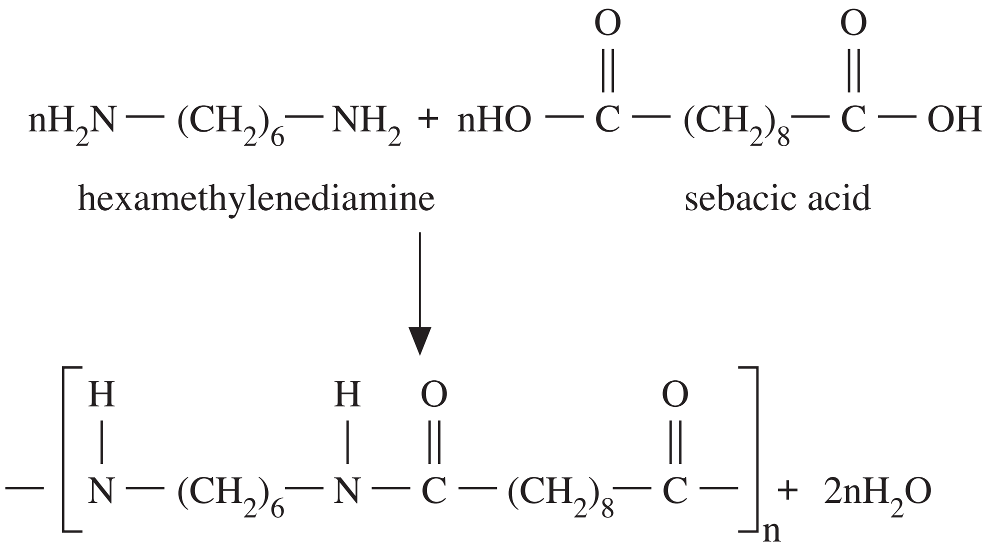
Chemically, nylons may be divided into **two categories**: those based on synthetic routes (1) and (2) for the synthesis of **nylon 6,6**; and those based on routes (3) and (4) for synthesis of **nylon 6**.

Since the polymerization reaction occurs above the melting points of both reactants and the polymer, the polymerization process is known as **melt polymerization**.



Other polyamides of commercial importance are nylons that are **higher analogs** of the more common types: nylons **11**; **12**; **6,10**; and **6,12**.

The numerals in the trivial names refer to the number of carbon atoms in the monomer(s). In designating A–A/B–B nylons, the **first number** refers to the **number of carbon atoms** in the **diamine**, while the **second number** refers to the total **number of carbon atoms** in the **diacid**.

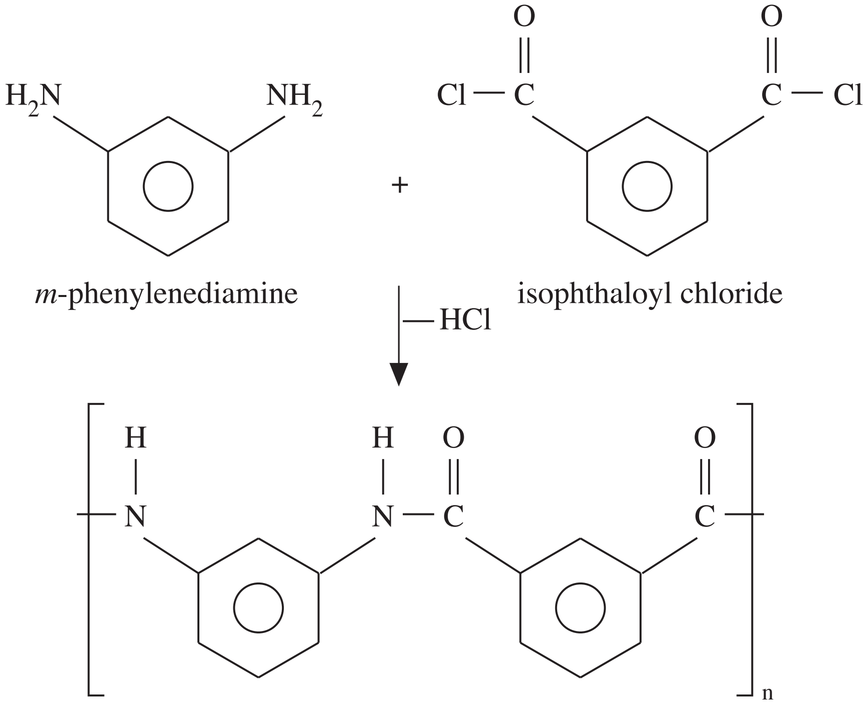


$$nH_2N-(CH_2)_6-NH_2 + nHO-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-OH \longrightarrow -\left[\underset{}{\overset{H}{\overset{|}{N}}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-\right]_n + 2nH_2O$$

poly(hexamethylene sebacamide)
(nylon 6,10)

In the 1960s, aromatic polyamides were developed to **improve** the **flammability** and **heat resistance** of nylons.

Poly(*m*-phenyleneisophthalamide), or **Nomex**, is produced via the **solution** or **interfacial polymerization**.

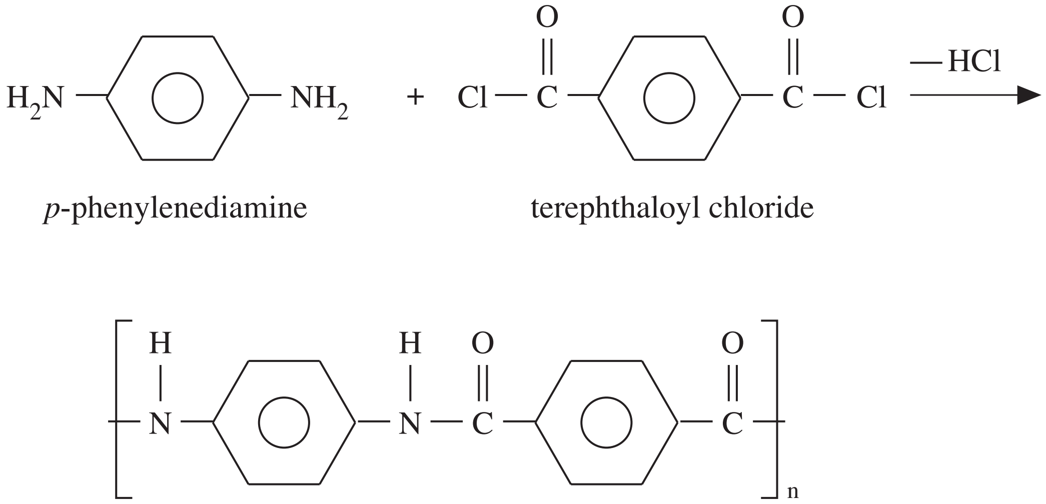


poly(*m*-phenyleneisophthalamide)
(Nomex)

The corresponding **linear aromatic polyamide** is **Kevlar aramid** which decomposes only above 500 °C.

The **high thermo-oxidative stability** of Kevlar is due to the absence of aliphatic units in its main chain.

The material is **highly crystalline** and forms a **fiber** whose **strength** and **modulus** are **higher** than that of **steel** on an equal weight basis.



p-phenylenediamine

terephthaloyl chloride

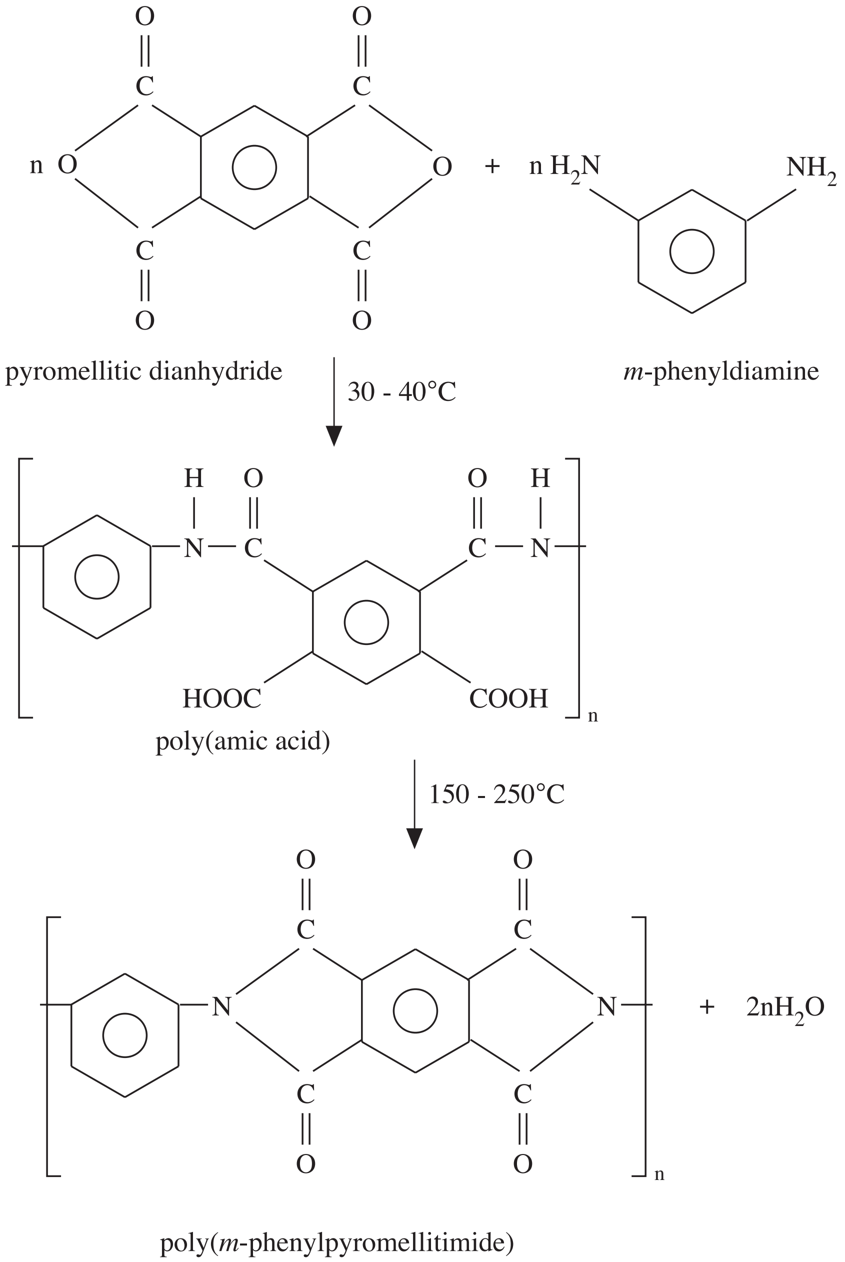
poly(*p*-phenyleneterephthalamide)
(Kevlar)

4. Polyimides

Polyimides are condensation polymers obtained from the reaction of dianhydrides with diamines.

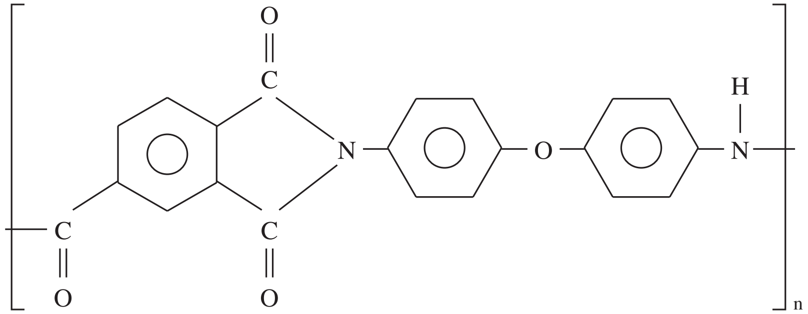
Aromatic polyimides are formed by a general two-stage process.

The cured or fully imidized polyimide is **insoluble** and **infusible** with high thermooxidative stability and **good electrical-insulation** properties.



For polyimides to be useful polymers, they must be processable, which means that they have to be meltable. Melt processability of polyimides can be improved by combining the basic imide structure with more **flexible** aromatic groups (aromatic ethers and amides).

Polyamide-imides (5) are obtained by condensing trimellitic anhydrides and aromatic diamines, while polyetherimides (6) are produced by nitro displacement reaction involving bisphenol A, 4,4′-methylenedianiline, and 3-nitrophthalic anhydride.



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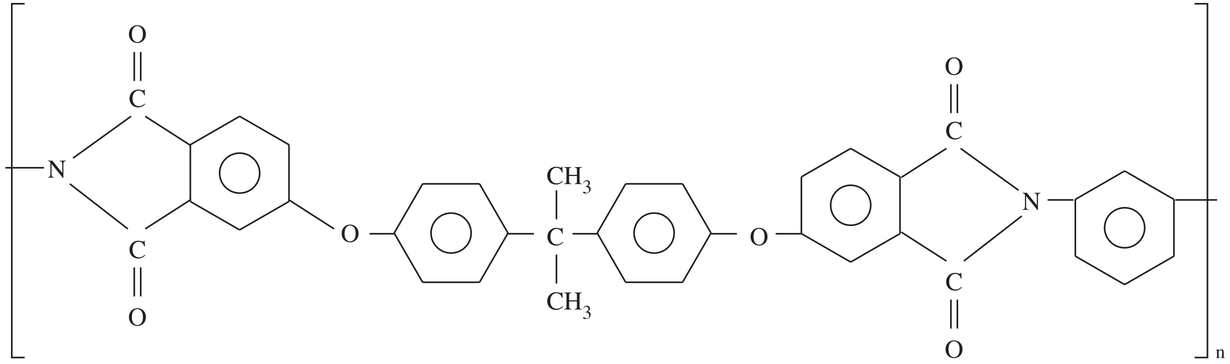

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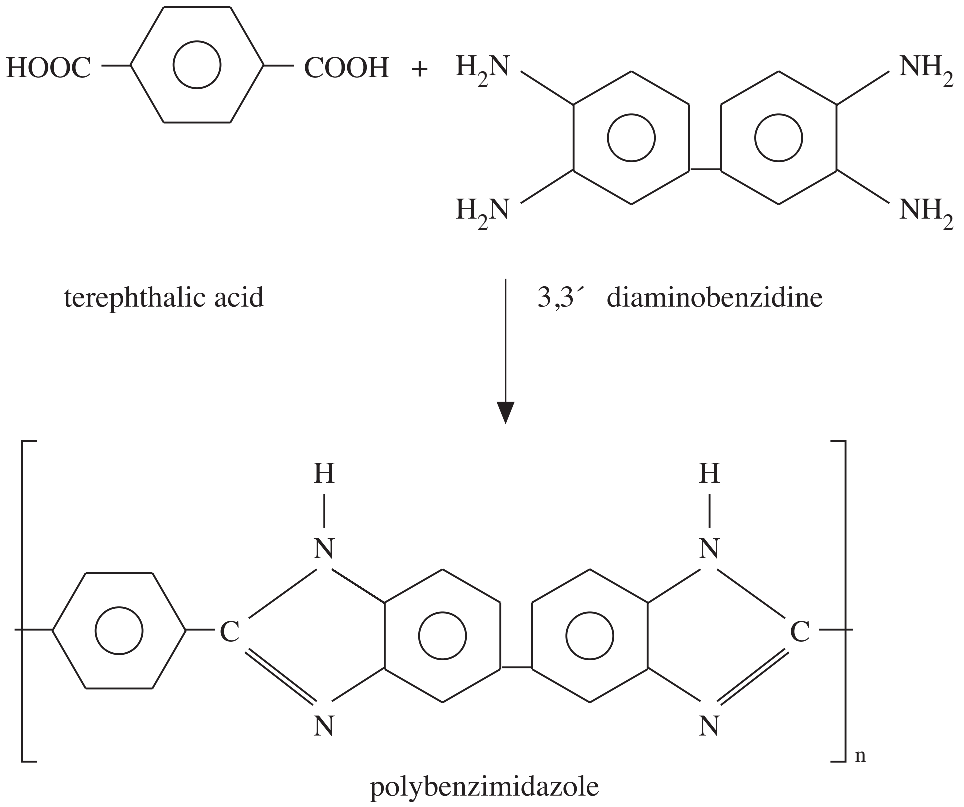
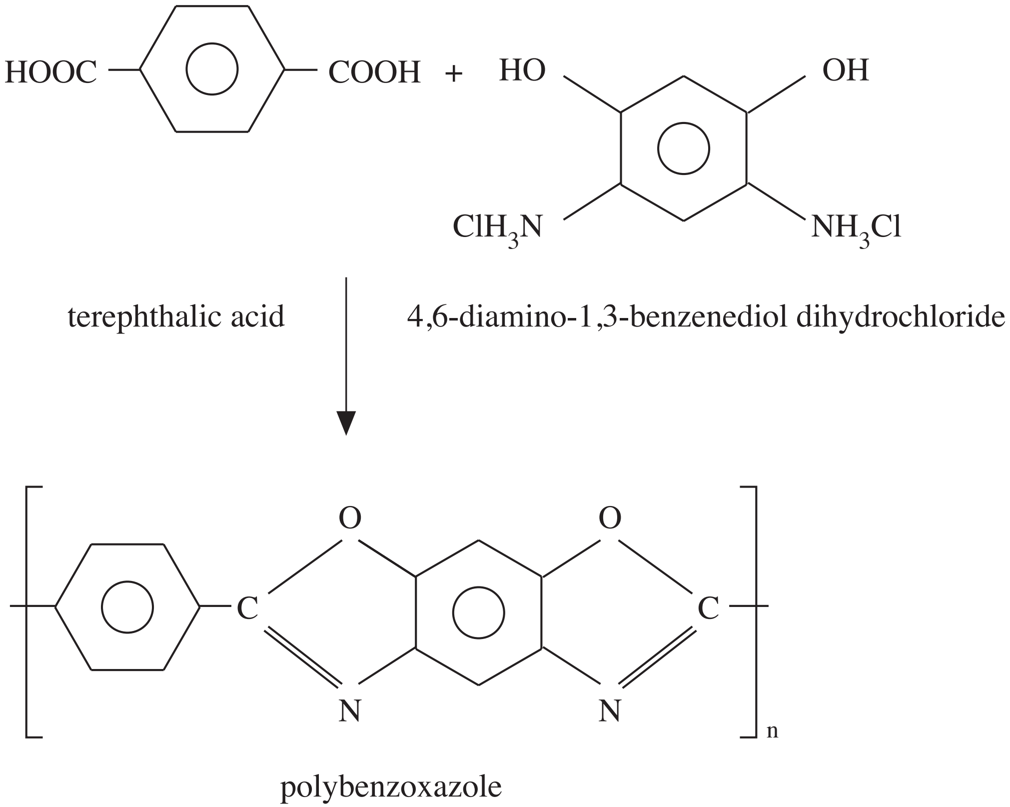
5. Polybenzimidazoles and Polybenzoxazoles

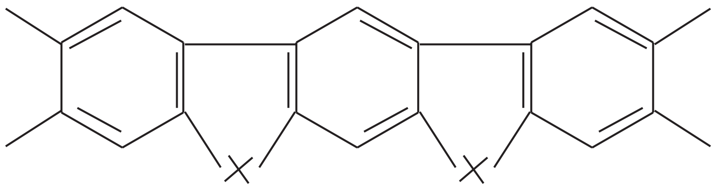
When the molar ratio of carboxyl groups (e.g., terephthalic acid) to amino groups (e.g., 3,3′ diaminobenzidine) is 1:2, polybenzimidazoles are formed; whereas where the molar ratio of carboxyl, amino, and hydroxyl groups is 1:1:1, polybenzoxazoles are formed.

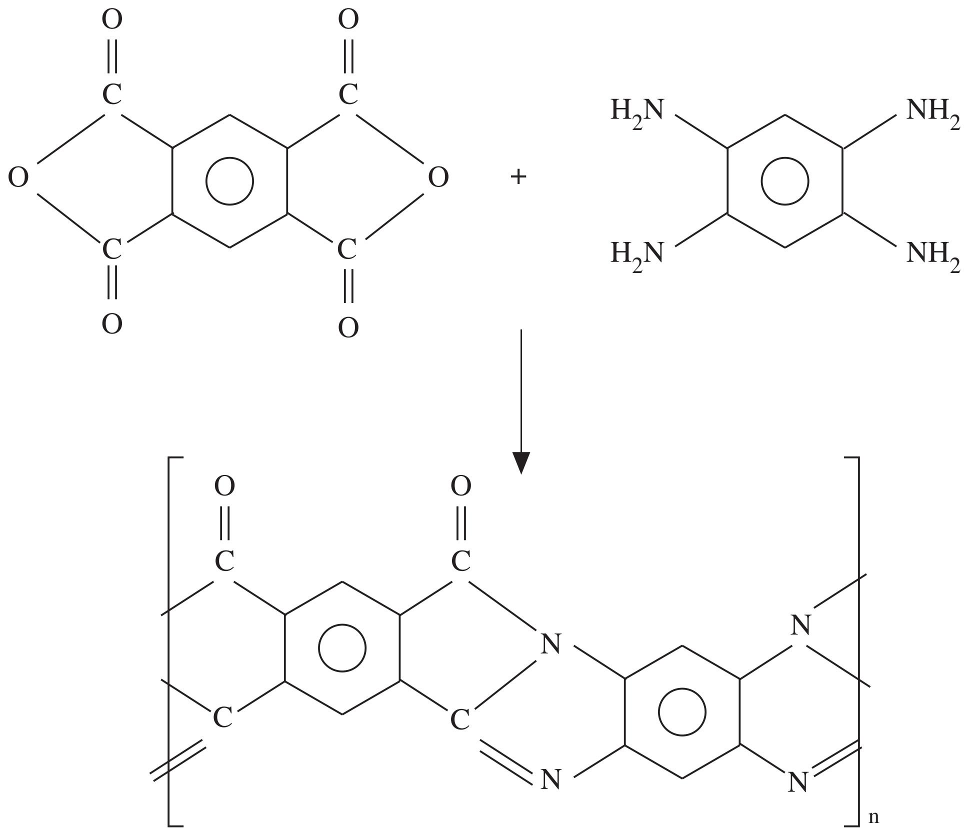




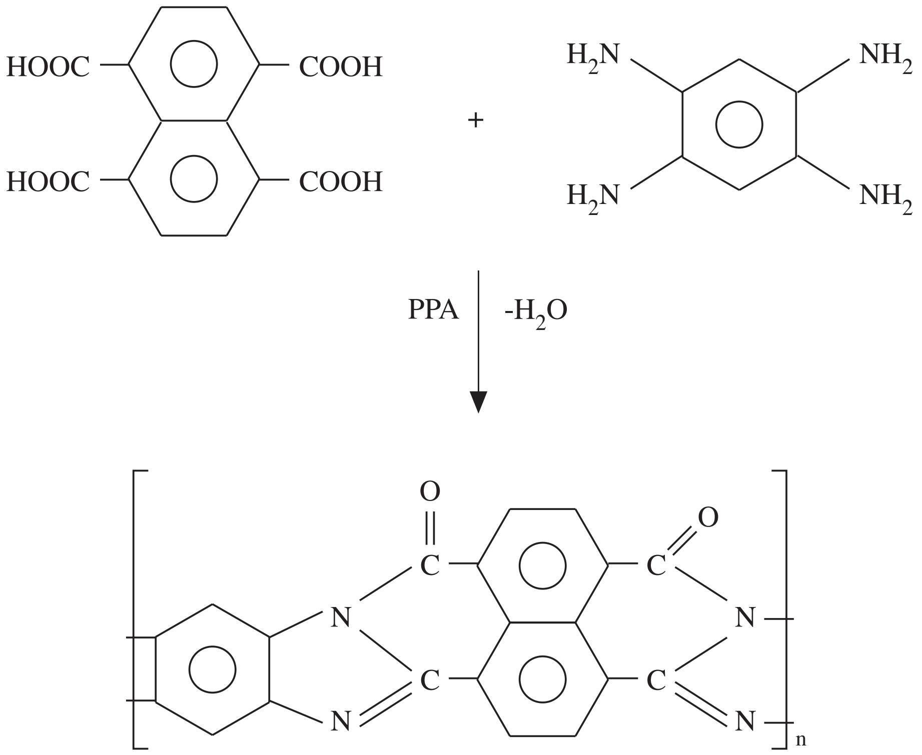
6. Aromatic Ladder Polymers

To increase the **rigidity** of linear macromolecules is the **elimination of single bonds** in the main chain so that it is **composed of** only condensed cyclic units (aromatic or cycloaliphatic, homocyclic or heterocyclic).





Polyquinoxalines are another group of ladder polyme



Ladder polymers are also referred to as “double-chain” or “double-strand” polymers because, unlike other polymers, the backbone consists of two chains.

For polymer degradation, two bonds must be broken in the same chain residue. Therefore, ladder polymers usually have exceptional thermal, mechanical, and electrical properties.

7. Formaldehyde Resins

Formaldehyde is employed in the production of **aminoplasts** and **phenoplasts**, which are two different but related classes of **thermoset** polymers.

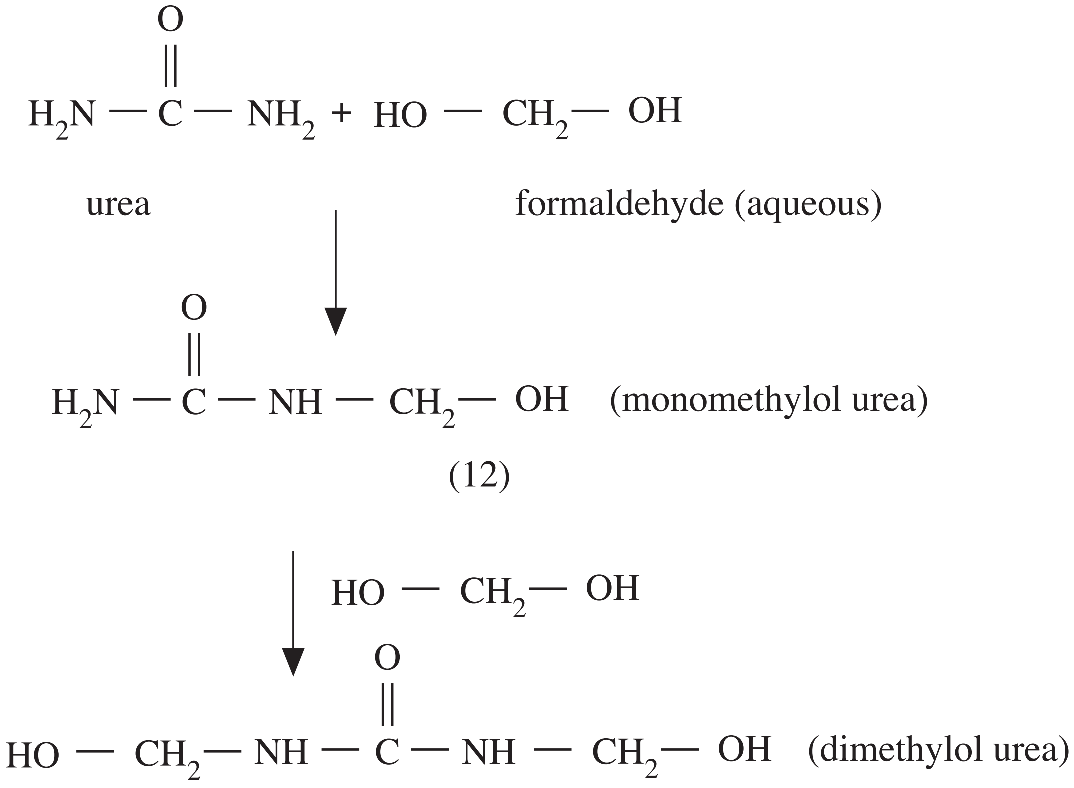
Aminoplasts are products of the condensation reaction between either urea (urea–formaldehyde or UF resins) or melamine (melamine–formaldehyde or MF resins) with formaldehyde.

Phenoplasts or phenolic (phenol–formaldehyde or PF) resins are prepared from the condensation products of phenol or resorcinol and formaldehyde.

a. Urea–Formaldehyde Resins

The synthesis consists basically of two steps. In the first step, urea reacts with aqueous formaldehyde under slightly alkaline conditions to produce methylol derivatives of urea.

In the second step, condensation reactions between the methylol groups occur under acidic conditions, leading ultimately to the formation of a network structure:



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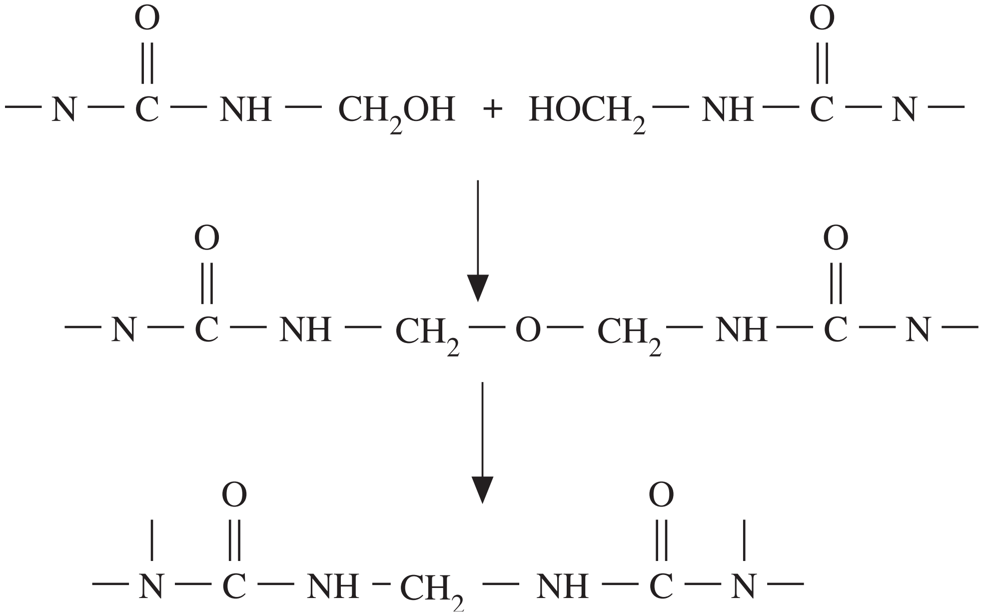
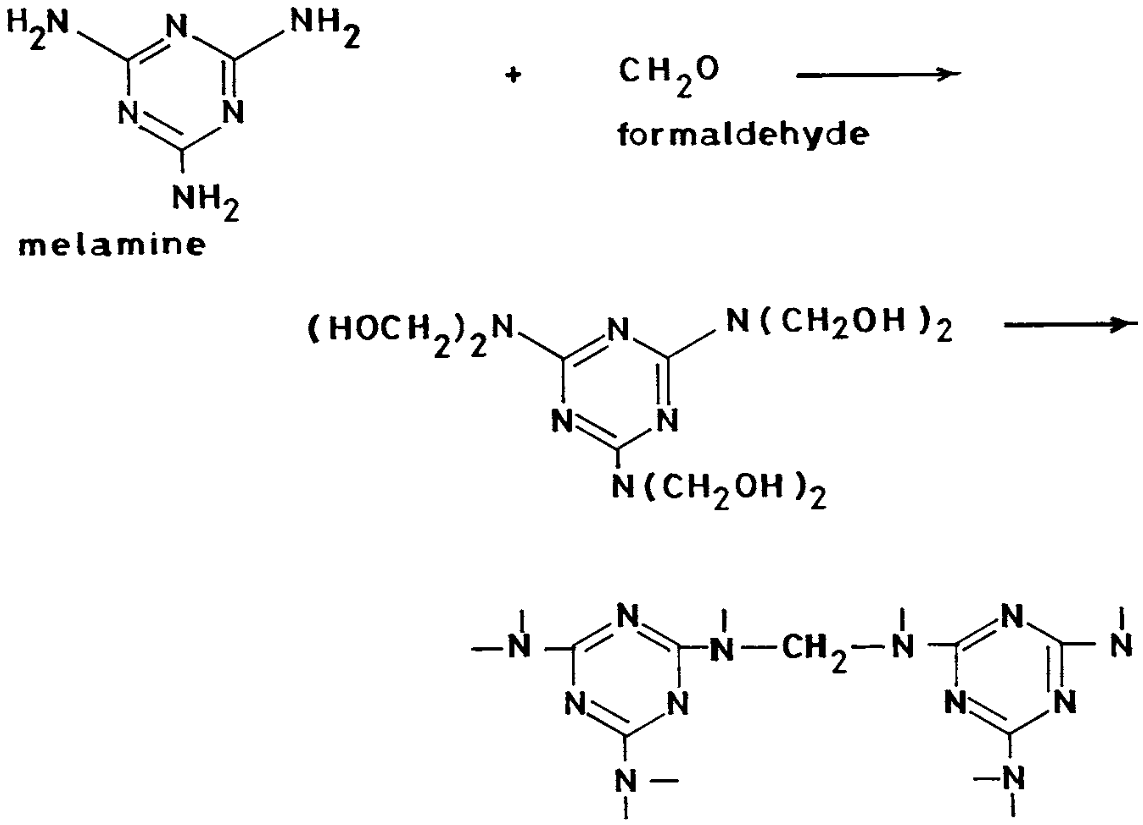


b. Melamine–Formaldehyde Resins

Production of melamine–formaldehyde polymers involves reactions essentially similar to those of UF resins, initially production of methylol derivatives of melamine, and subsequently condensation form methylene bridges between melamine groups in a rigid network structure.

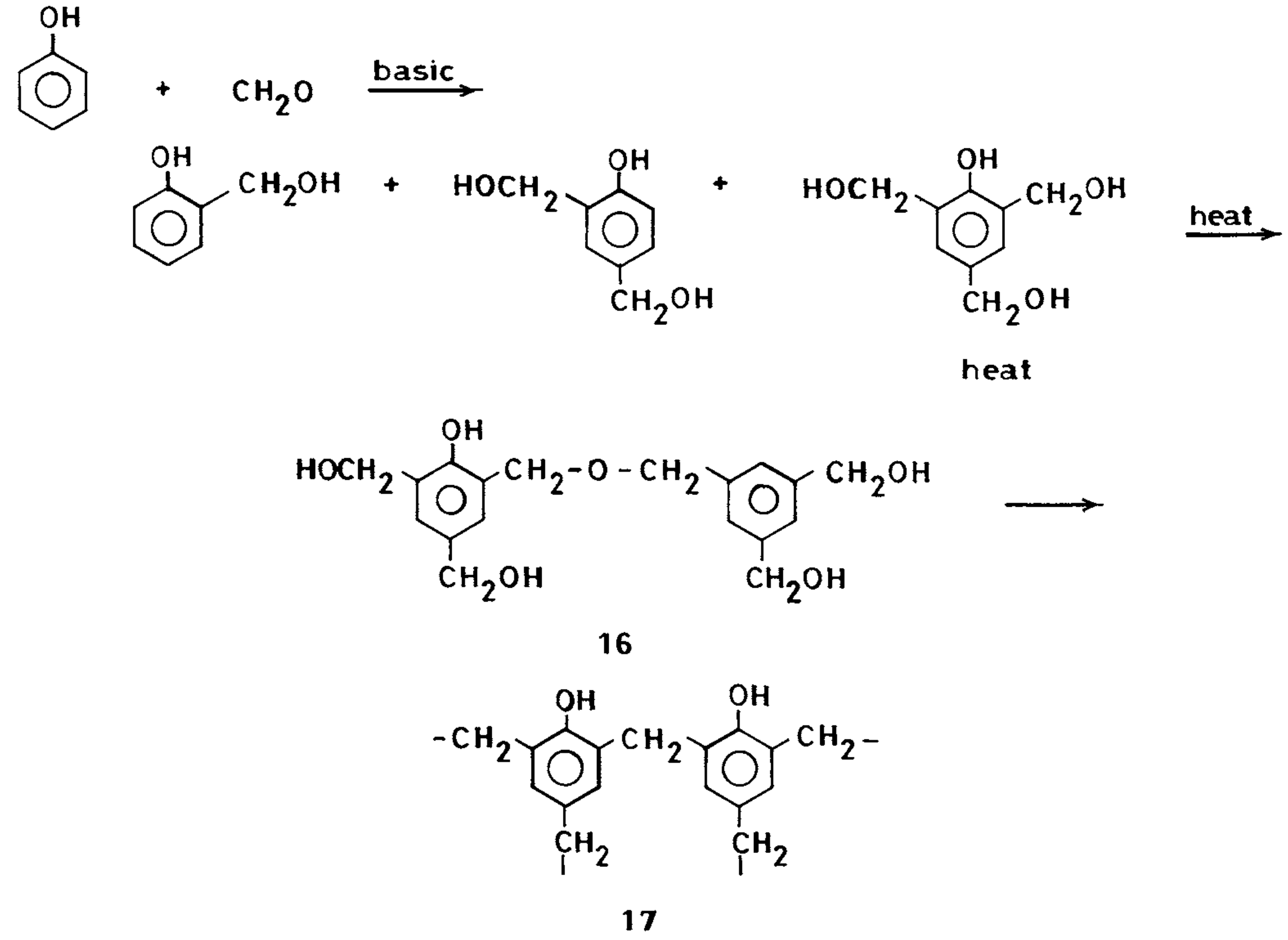


c. Phenol–Formaldehyde Resins

Phenolic resins are prepared by either **base-catalyzed** (**resoles**) or **acid-catalyzed** (**novolacs**) addition of formaldehyde to phenol.

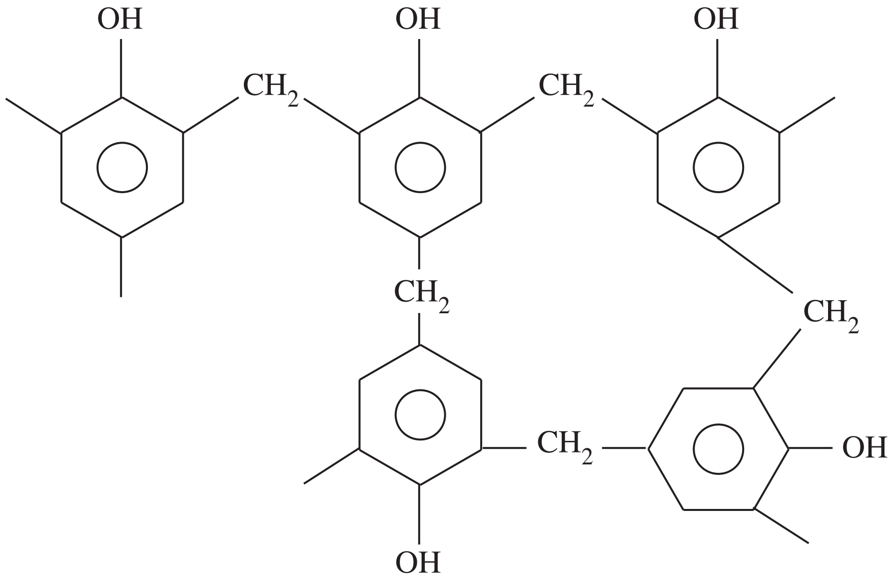
In the preparation of resoles, phenol and excess formaldehyde react to produce a mixture of methylol phenols. These condense on heating to yield soluble, low-molecular-weight prepolymers or resoles (16).

On heating of resoles at elevated temperature under basic, neutral, or slightly acidic conditions, a high-molecular-weight network structure or phenolic rings linked by methylene bridges (17) is produced.


basic
heat
heat
16
17

Novolacs are low-molecular-weight, fusible but insoluble prepolymers (18) prepared by reaction of formaldehyde with molar excess of phenol.

Novolacs, unlike resoles, do not contain residual methylol groups. A high-molecular-weight network polymer similar to that of resoles is formed by heating novolac with additional formaldehyde, paraformaldehyde, or hexamethylenetetramine.



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8. Polyethers

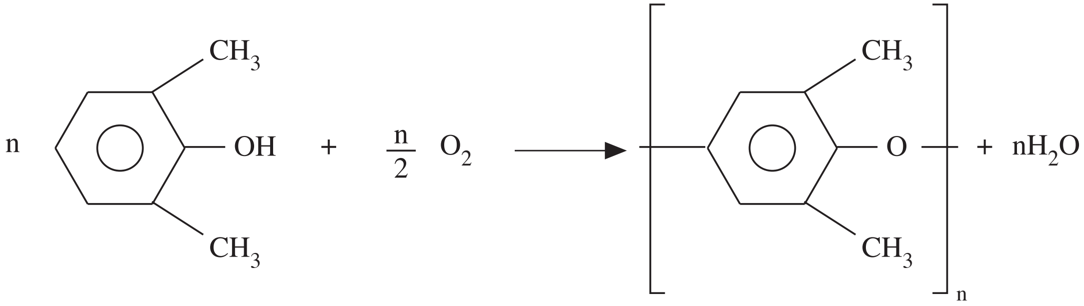
The introduction of aromatic units into the main chain results in polymers with better thermal stability than their aliphatic analogs.

Poly(phenylene oxide), PPO, has many attractive properties, including high-impact strength, resistance to attack by mineral and organic acids, and low water absorption.

It is used, usually **blended** with **high-impact polystyrene** (HIPS), to ease processability in the manufacture of machined parts and business machine enclosures.

PPO is obtained from free-radical, step-growth, oxidative coupling of 2,6-dimethylphenol (2,6-xylenol).

This involves passing oxygen into a reaction mixture containing 2,6-xylenol, cuprous chloride, and pyridine.

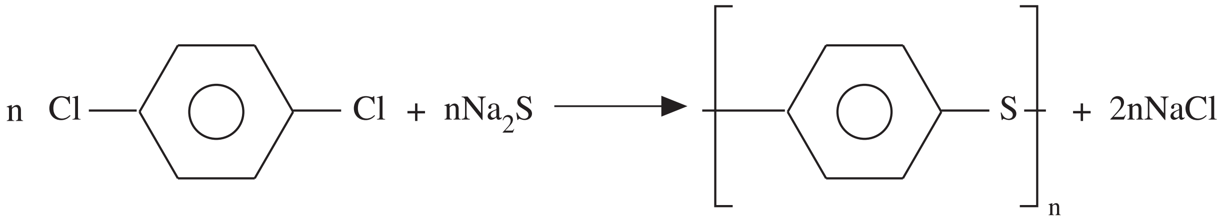


9. Polysulfides

Aromatic polythioethers or polysulfides are closely related to polyethers in structure and properties.

poly(phenylene sulfide) (PPS) is used as electrical insulators and structural parts in the building of engines and vehicles.

PPS is prepared by the condensation reaction between *p*-dichlorobenzene and sodium sulfide:

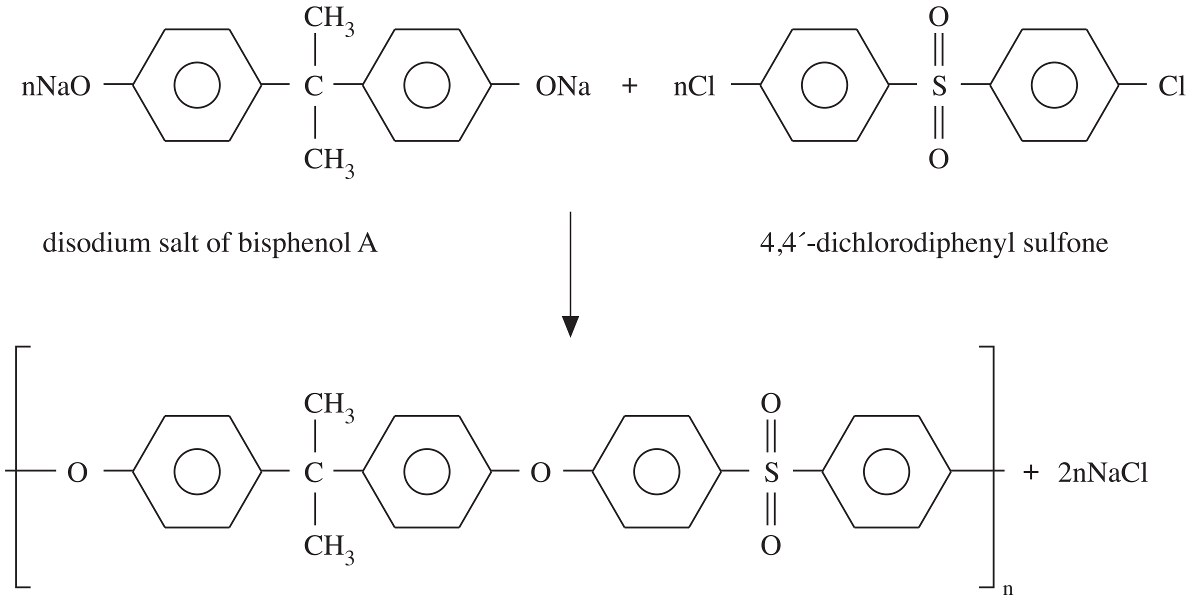


10. Polysulfones

Polysulfones are tough, high-temperature-resistant engineering thermoplastics.

Polysulfones may be synthesized by the nucleophilic substitution of alkali salts of biphenates with activated aromatic dihalides.

A typical example is the preparation of bisphenol A polysulfone from the reaction of disodium salt of bisphenol A with dichlorodiphenyl sulfone:



V. RING-OPENING POLYMERIZATION

While ring-opening polymerization shares certain features with condensation and addition polymerization mechanisms, it differs from each of them in at least one important respect.

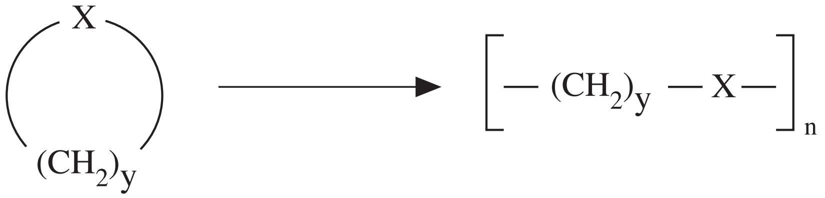
First, in contrast to condensation polymerization, no small molecule is split off in ring-opening polymerization. **Second**, unlike olefin polymerization, the driving force for ring-opening polymerization is not derived from the loss of unsaturation.

A significant number of polymers has been produced from the ring-opening of cyclic organic compounds: epoxides such as ethylene and propylene oxides and epichlorohydrin and other cyclic ethers like trioxane and tetrahydrofuran, and cyclic esters (lactones), cyclic amides (lactams), cycloolefins, and siloxane.

Ring-opening polymerization involves essentially an **initial ring-opening** of the cyclic monomer **followed by polyaddition**. The resulting polymers are normally **linear**.

Their **structural units** usually have the **same composition** as the **monomer**.

Major applications of polymers obtained from ring-opening polymerization: coatings, fibers, elastomers, adhesives, and thermoplastics- and thermoset-based composite systems.

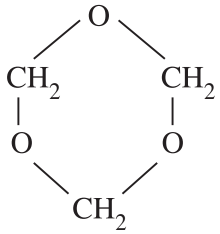
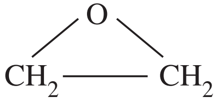
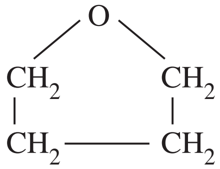
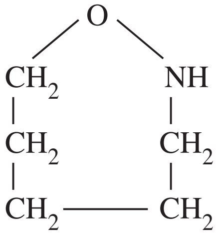
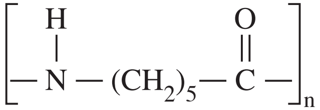
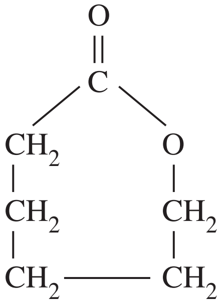
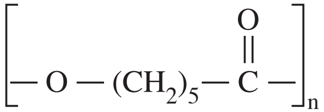
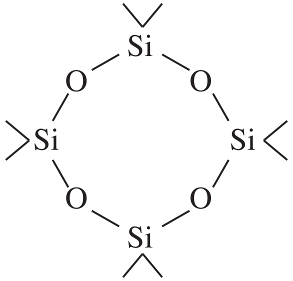
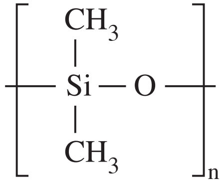


X may be a heteroatom such as O, S, or a group like NH, –O–CO–, –NH–CO, or –C=C–.

Not all cyclic compounds can undergo ring-opening polymerization.

The **nature of X** is such that it **provides a mechanism** for a catalyst or initiator to form the initiating coordination intermediate with the cyclic ring.

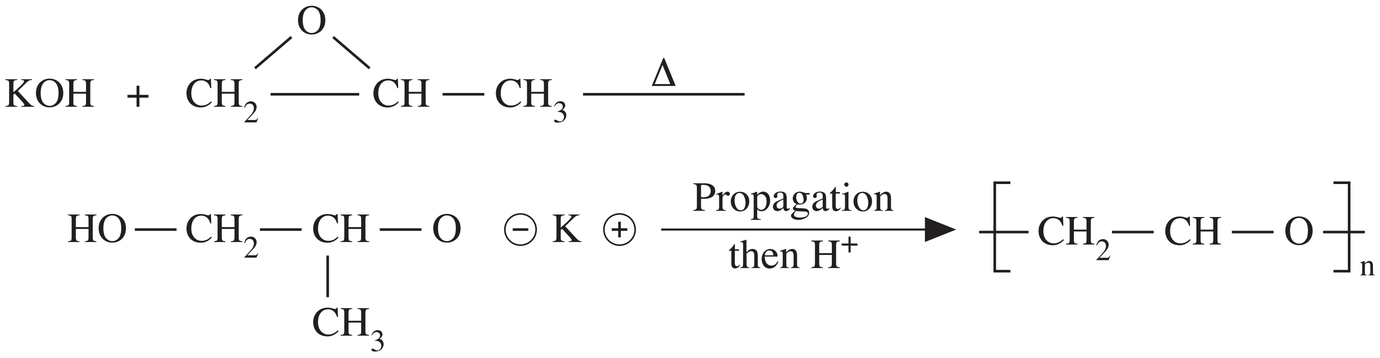
Table 2.4 *Examples of Commercially Important Ring-Opening Polymerizations*

Monomer	Polymer	Mechanism
 trioxane	$\left[-CH_2-O-\right]_n$ polyoxymethylene	Cationic
 ethylene oxide	$-\left[CH_2-CH_2-O-\right]_n$ poly(ethylene oxide)	Anionic, cationic, coordination
 tetrahydrofuran	$-\left[(CH_2)_4-O-\right]_n$ poly(tetramethylene oxide)	Cationic
 Caprolactam	 $\left[-\overset{\overset{\displaystyle H}{\vert}}{N}-(CH_2)_5-\overset{\overset{\displaystyle O}{\Vert}}{C}-\right]_n$ Polycaprolactam (nylon 6)	Hydrolytic, anionic
 caprolactone	 $\left[-O-(CH_2)_5-\overset{\overset{\displaystyle O}{\Vert}}{C}-\right]_n$ polycaprolactone	Anionic, cationic
 Dimethysiloxane (cyclic tetramer)	 $\left[-\underset{\underset{\displaystyle CH_3}{\vert}}{\overset{\overset{\displaystyle CH_3}{\vert}}{Si}}-O-\right]_n$ poly(dimethylsiloxane)	Anionic, cationic

A. POLY(PROPYLENE OXIDE)

The polymerization of propylene oxide represents an important example of industrial ring-opening polymerization.

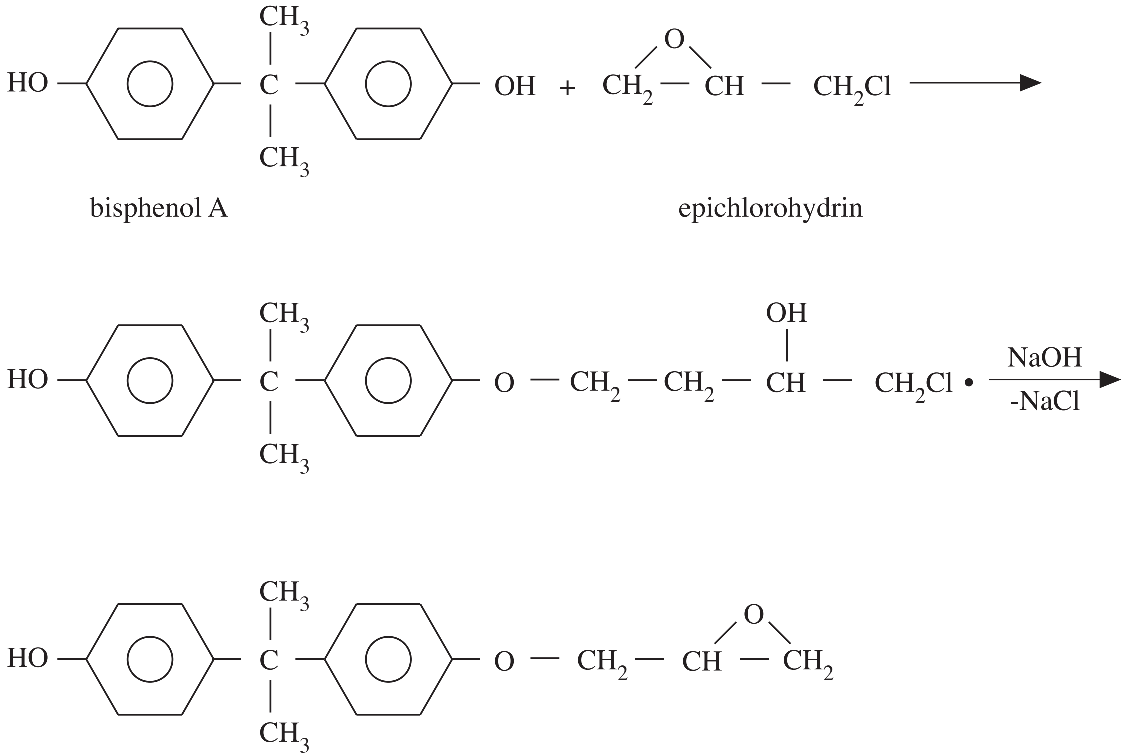
It involves an attack of the least sterically hindered carbon by the hydroxyl anion to produce the alkoxide. This produces essentially linear polymer molecules.



Poly(propylene oxide) glycols are utilized extensively as soft segments in urethane foams, which are used as automobile seats.

B. EPOXY RESINS

Epoxy resins are normally prepared by the base-catalyzed reaction between an epoxide such as epichlorohydrin and a polyhydroxy compound such as bisphenol A:



The molar ratio of epichlorohydrin to bisphenol A can range from as high as 10:1 to as low as 1.2:1.

This produces resins ranging from liquid to semisolid to solid and varying molecular weights and softening points.

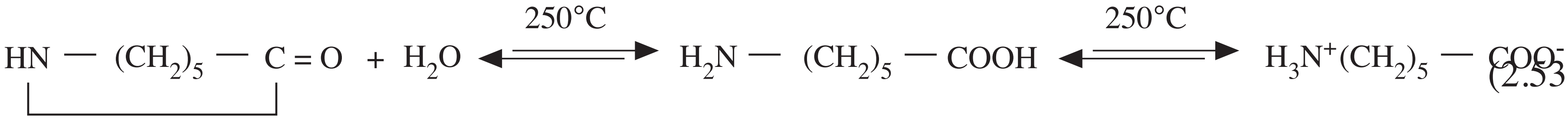
The products are oligomers or prepolymers, which are hardly used as such; they have pendant hydroxyl groups and terminal epoxy groups.

The epoxy prepolymer can be cross-linked or cured by reaction with a number of reagents, including primary and secondary amines.

C. POLYCAPROLACTAM (NYLON 6)

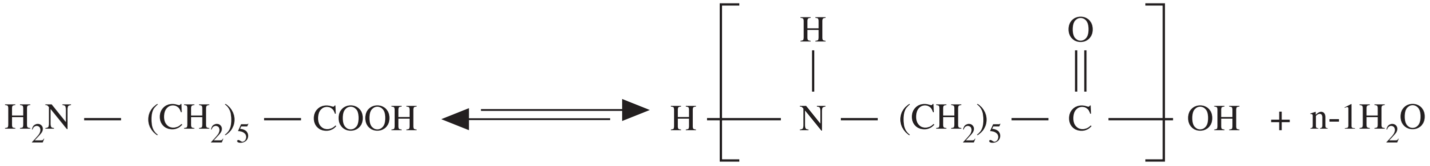
The industrial manufacture of nylons involves either water-initiated (hydrolytic) or a strong base-initiated (anionic) polymerization of caprolactam.

Hydrolytic polymerization of caprolactam is the most important commercial process for the production of nylon 6:



$$HN-(CH_2)_5-C=O + H_2O \overset{250°C}{\rightleftharpoons} H_2N-(CH_2)_5-COOH \overset{250°C}{\rightleftharpoons} H_3N^+(CH_2)_5-COO^-$$

(2.53)



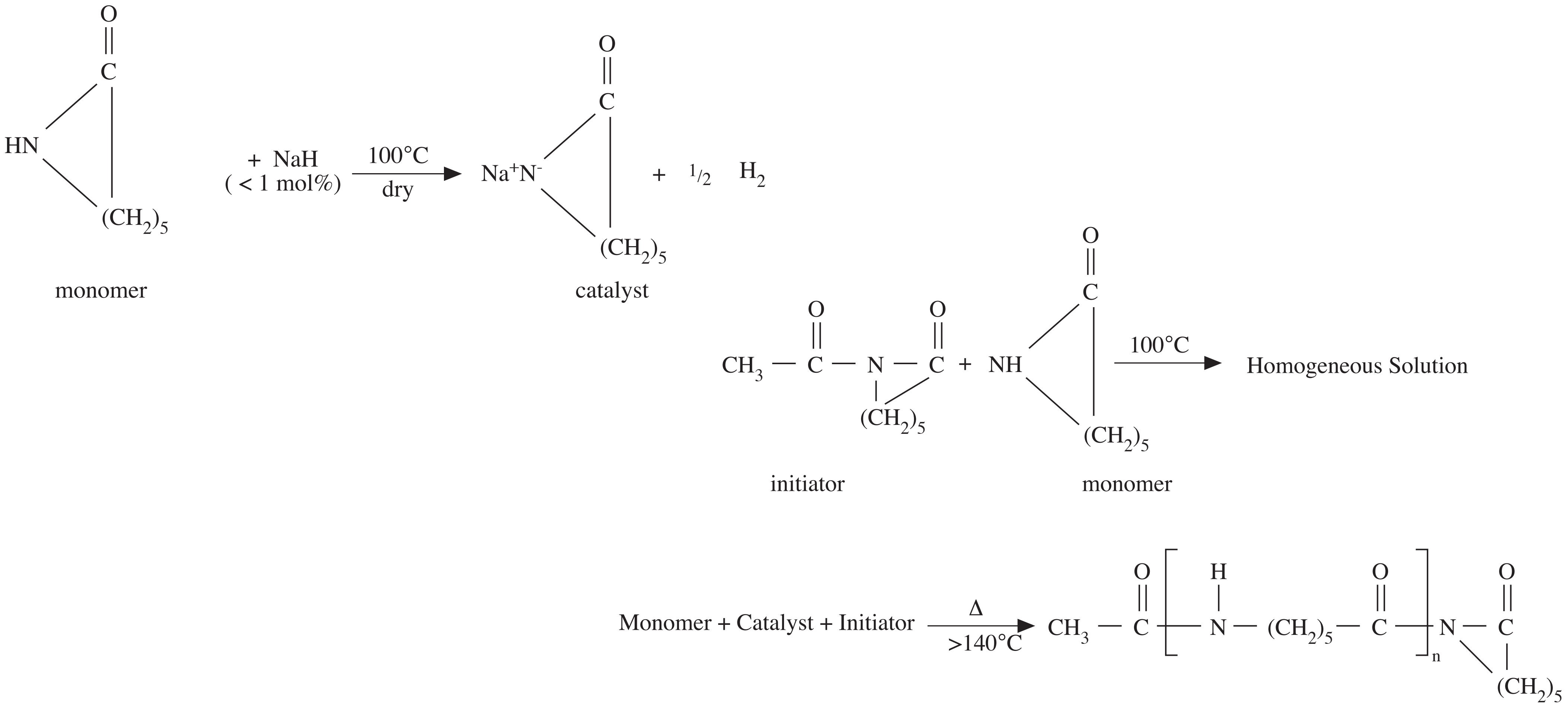
$$H_2N-(CH_2)_5-COOH \rightleftharpoons H\left[\overset{H}{\overset{|}{N}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}\right]OH + n\text{-}1H_2O$$

(2.54)

Water opens the caprolactam ring producing aminocaproic acid, which is believed to exist as the zwitterion. The zwitterion interacts with and initiates the step polymerization of the monomer, with the ultimate generation of linear polymer molecules.

In other words, the polymerization process involves an initial ring-opening of the monomer that is followed by the step polymerization.

This polymerization is usually carried out in a two-stream reactor in which one stream contains the catalyst dissolved in the monomer and the second stream contains the initiator dissolved separately in the monomer:



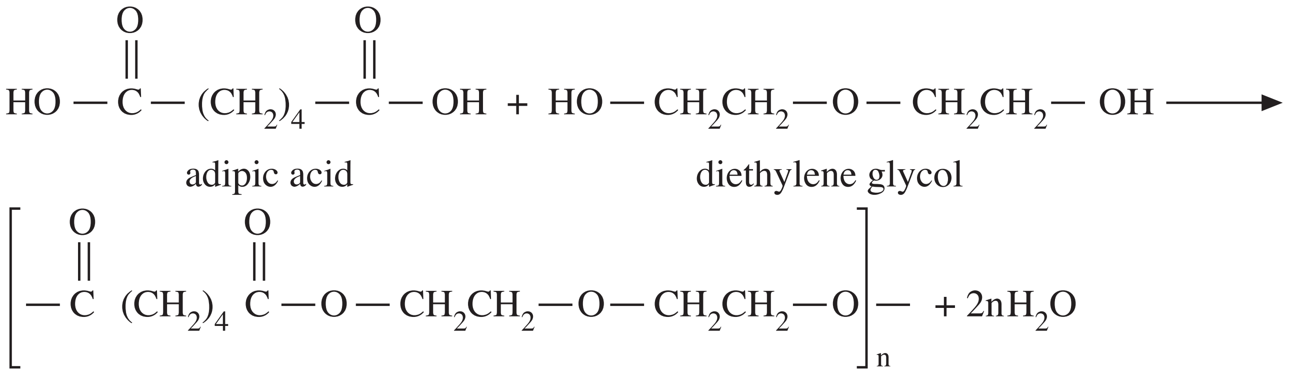
KINETICS OF CONDENSATION POLYMERIZATION

The mechanism of polycondensation reactions is thought to parallel that of the low-molecular-weight analogs. It is assumed that all steps in a condensation polymerization have equal rate constants. Consider esterification:

Case 1: Polymerization without Added Strong Acid: the formation of a polyester from a glycol and a dibasic acid. This polyesterification and other simple esterifications are acid-catalyzed. In the absence of an added strong acid, a **second molecule** of the acid being esterified **acts as the catalyst**.

The rate of polyesterification process can be written where concentrations are expressed as equivalents of the functional groups.

The rate constant k is independent of molecular size of reacting species and is the same for all functional groups.



$$HO-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-OH + HO-CH_2CH_2-O-CH_2CH_2-OH \longrightarrow$$

$$\left[-\overset{\overset{\displaystyle O}{\|}}{C}\ (CH_2)_4\ \overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2CH_2-O-CH_2CH_2-O\right]_n- \ + 2nH_2O$$

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

If the concentration, C, of the unreacted carboxyl and hydroxyl groups at time t are equal, the rate equation may be rewritten as: (third-order kinetic expression)

$$\frac{-dc}{dt} = kc^3$$

On integration, this yields the third-order reaction expression: $2kt = \frac{1}{c^2} - \text{constant}$

To introduce the ***extent of reaction****,* p, defined as the **fraction** of the functional group that has reacted at time t. That is,

$$p = \frac{C_o - C}{C_o}$$

where C_o = initial concentration of one of the reactants: $C = C_o(1-p)$

Hence, on substitution, the rate equation becomes $2C_o^2kt = \frac{1}{(1-p)^2} - 1$

A plot of $1/(1-p)^2$ against time should be **linear**. The quantity 1/(1-p) is called the degree of polymerization, **DP**, which it corresponds to the average number of monomer molecules in the chain.

Case II: Polymerization with Added Strong Acid: The kinetic expression can be greatly simplified if the polyesterification is carried out in the presence of a small amount of strong acid, e.g., *p*-toluene sulfonic acid. With the catalyst concentration kept constant throughout the process, the rate expression becomes:

$$\frac{-dc}{dt} = k'c^2$$

where k′ = k[catalyst] and where the alcohol and carboxylic acid concentrations are kept constant. Integrating this second-order rate equation and inserting the extent of reaction, p, we have:

$$C_o k' t = \frac{1}{1-p} - 1$$

It shows the linear relation between 1/(1-p) and time.

STOICHIOMETRY IN LINEAR SYSTEMS

At any stage of the polymerization process, each molecule will be terminated on either side by an unreacted functional group. Therefore, the number of molecules present can be determined by measuring the **number of structural units per molecule**, i.e., the **number-average degree of polymerization**, X_n, is given by the ratio of the initial number of molecules to the final number of molecules, i.e.,

$$\overline{X}_n = \frac{\text{original number of molecules}}{\text{final number of molecules}}$$

$$= \frac{C_o}{C_o\left(1-p\right)} = \frac{1}{1-p}$$

From the definition of X_n, it follows that the number-average molecular weight will be given by the expression: where M_o = average molecular weight of the structural unit.

$$\overline{M}_n = \overline{X}_n M_o = \frac{M_o}{1-p}$$