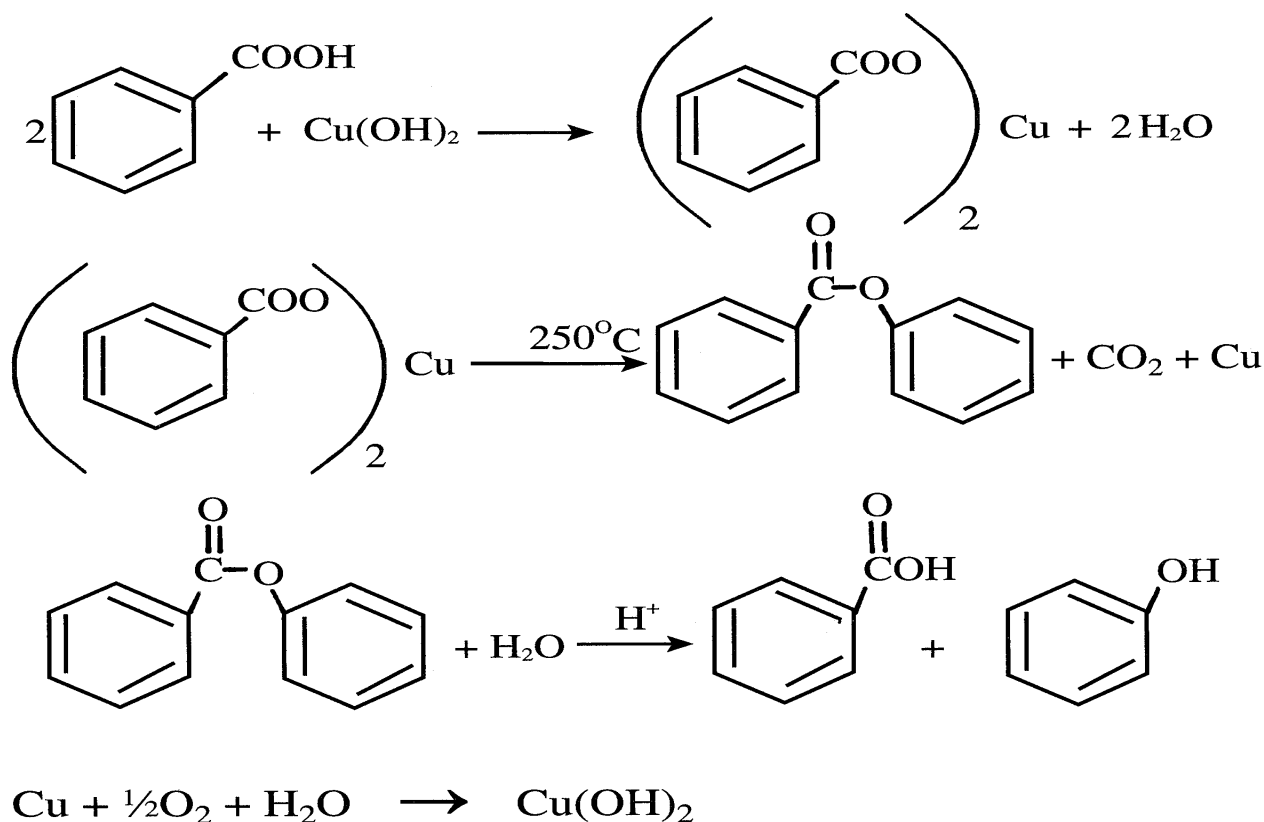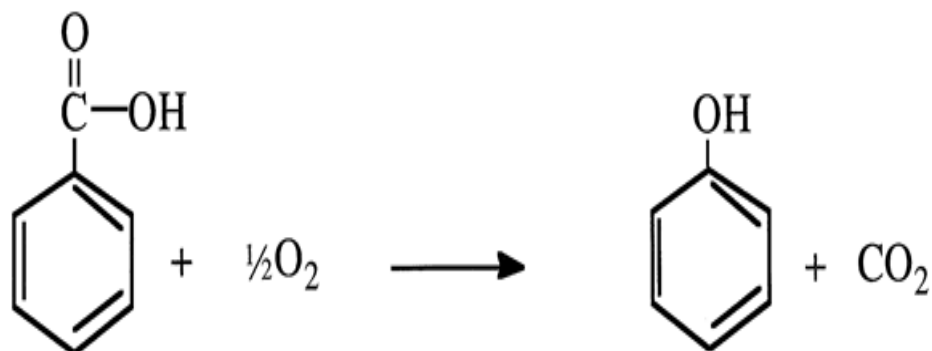# Lecture Twelve

Phenol from Benzoic Acid

The action of a copper salt converts benzoic acid to phenol. The copper, reoxidized by air, functions as a real catalyst. The process operates in the vapor phase at approximately 250°C. Phenol yield of 90% is possible:

$$2 \; C_6H_5COOH + Cu(OH)_2 \longrightarrow (C_6H_5COO)_2Cu + 2\,H_2O$$

$$(C_6H_5COO)_2Cu \xrightarrow{250°C} C_6H_5\text{--}CO\text{--}O\text{--}C_6H_5 + CO_2 + Cu$$

$$C_6H_5\text{--}CO\text{--}O\text{--}C_6H_5 + H_2O \xrightarrow{H^+} C_6H_5COOH + C_6H_5OH$$

$$Cu + \tfrac{1}{2}O_2 + H_2O \longrightarrow Cu(OH)_2$$

The overall reaction is

the reaction occurs in the liquid phase at approximately 220–240°C over $Mg^{2+} + Cu^{2+}$ benzoate.
Magnesium benzoate is an initiator, with the Cu^{2+} reduced to Cu^{1+}. The copper (1) ions are reoxidized to copper (II) ions.
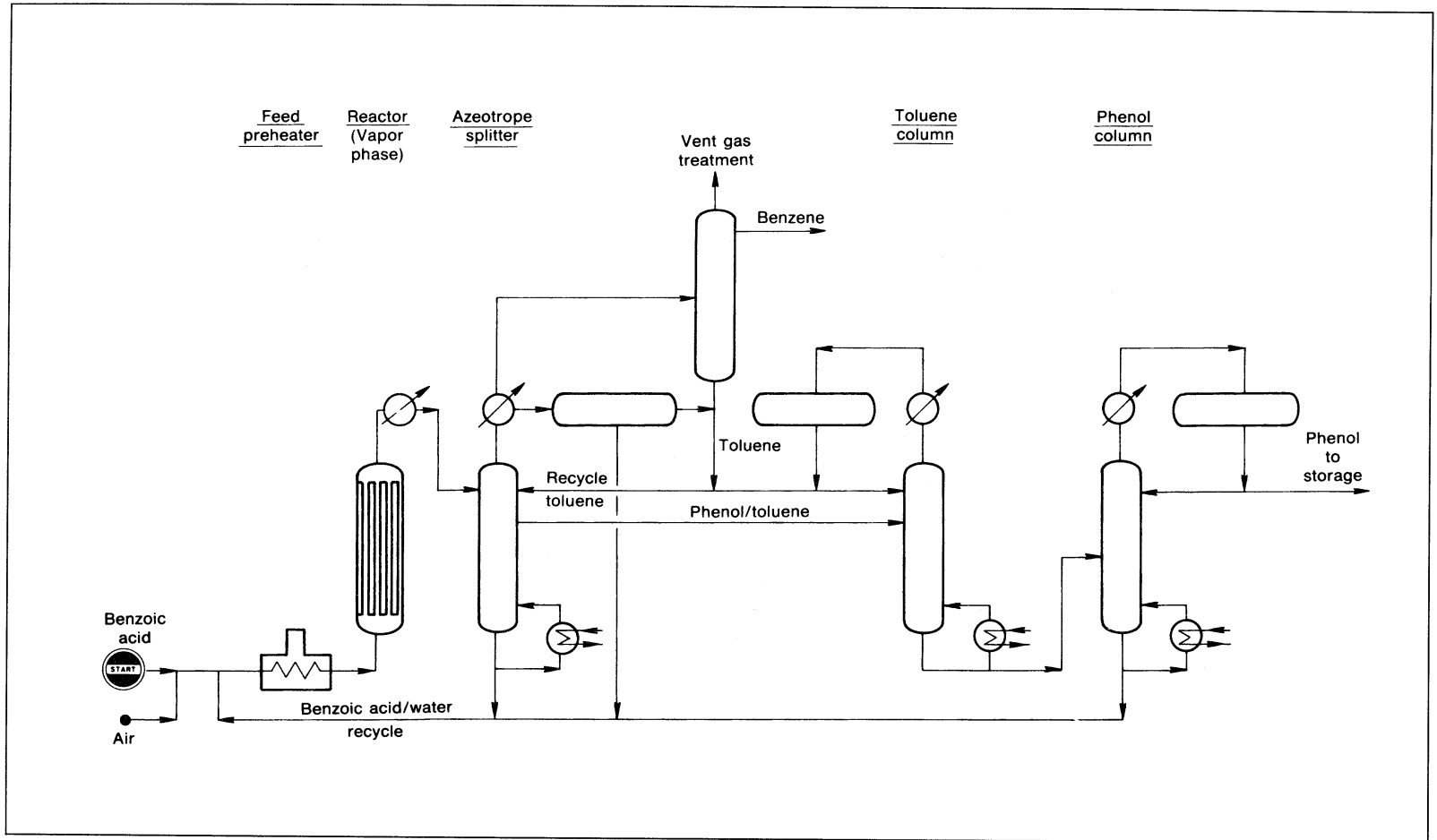
Figure 10-15. The Lummus benzoic-acid-to-phenol process.
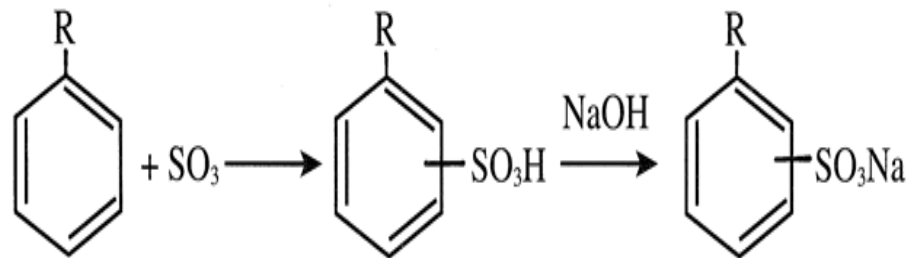
Linear Alkylbenzene

Linear alkylbenzene (LAB) is an alkylation product of benzene used to produce biodegradable anionic detergents. The alkylating agents are either linear C_{12}–C_{14} mono-olefins or monochloroalkanes. The linear olefins (alpha olefins) are produced by polymerizing ethylene using Ziegler catalysts or by dehydrogenating n-paraffins extracted from kerosines. Monochloroalkanes, on the other hand, are manufactured by chlorinating the corresponding n-paraffins. Dehydrogenation of n-paraffins to monoolefins using a newly developed dehydrogenation catalyst . The new catalyst is highly active and allows a higher per-pass conversion to monoolefins. Because the dehydrogenation product contains a higher concentration of olefins for a given alkylate production rate, the total hydrocarbon feed to the HF alkylation unit is substantially reduced.

Alkylation of benzene with linear monoolefins is industrially preferred.

(Figure 10-9) combines the dehydrogenation of n-paraffins and the alkylation of benzene. Monoolefins from the dehydrogenation section are introduced to a fixed-bed alkylation reactor over a heterogeneous solid catalyst. Older processes use HF catalysts in a liquid phase process at a temperature range of 40–70°C. The general alkylation reaction of benzene using alpha olefins could be represented as:

Linear alkylbenzene (LAB)
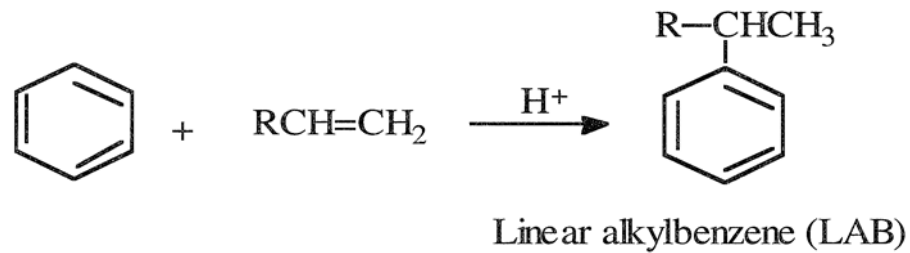
Detergent manufacturers buy linear alkylbenzene, sulfonate it with SO_3, and then neutralize it with NaOH to produce linear alkylbenzene sulfonate(LABS), the active ingredient in detergents:
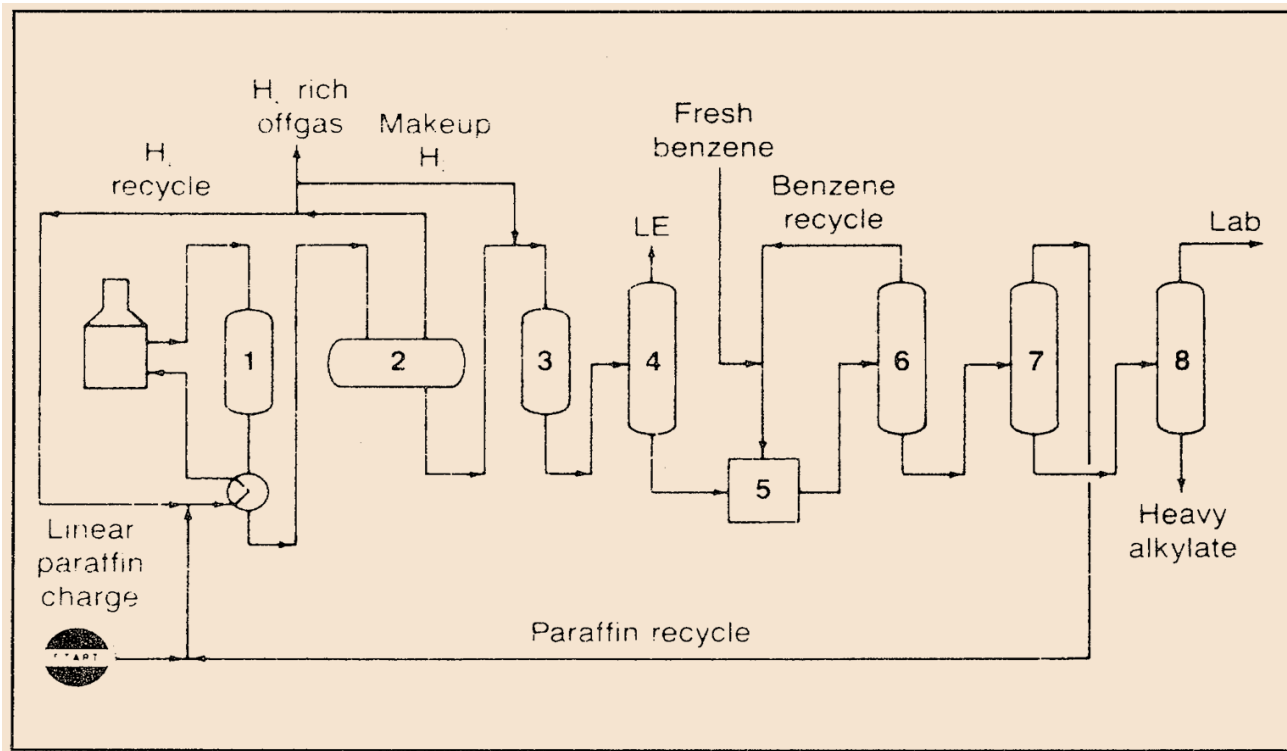
**Figure 10-9.** The UOP (Detal) process for producing linear alkylbenzene: •pacol dehydrogenation reactor, (2) gas-liquid separation, (3) reactor for convertingdiolefins to monoolefins, (4) stripper, (5) alkylation reactor, (6,7,8) fractionators.

# NITRATION OF BENZENE (Nitrobenzene [$C_6H_5NO_2$])

Similar to the alkylation and the chlorination of benzene, the nitration reaction is an electrophilic substitution of a benzene hydrogen (a proton) with a nitronium ion (NO_2^+). The liquid-phase reaction occurs in presence of both concentrated nitric and sulfuric acids at approximately 50°C.

Concentrated sulfuric acid has two functions: it reacts with nitric acid to form the nitronium ion, and it absorbs the water formed during the reaction, which shifts the equilibrium to the formation of nitrobenzene:

$$HNO_3 + 2H_2SO_4 \longrightarrow 2\ HSO_4^- + H_3O^+ + NO_2^+$$
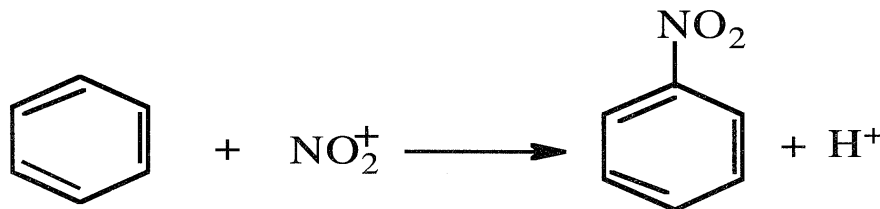
Most of the nitrobenzene ($\approx$97%) produced is used to make aniline. Other uses include synthesis of quinoline, benzidine, and as a solvent for cellulose ethers.

HYDROGENATION OF BENZENE
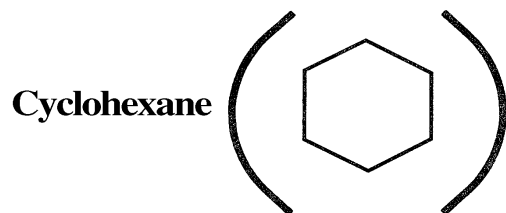
Cyclohexane

The hydrogenation of benzene produces cyclohexane. Many catalyst systems, such as Ni/alumina and Ni/Pd, are used for the reaction. General reaction conditions are 160–220°C and 25–30 atmospheres. Higher temperatures and pressures may also be used with sulfided catalysts:

$$+3H_2 \longrightarrow \qquad \Delta H = -266 \text{ KJ/mol}$$
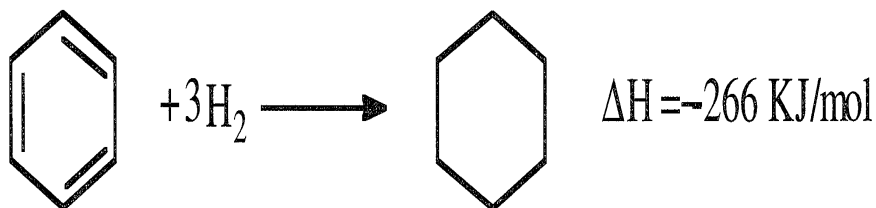
Older methods use a liquid phase process (Figure 10-11).New gas phase processes operate at higher temperatures with noble metal catalysts.

Using high temperatures accelerates the reaction (faster rate).The hydrogenation of benzene to cyclohexane is characterized by a highly exothermic reaction and a significant decrease in the product volume(from 4 to 1). Equilibrium conditions are therefore strongly affected by temperature and pressure. Figure 10-12 shows the effect of H_2/benzene mole ratio on the benzene content in the products. It is clear that benzene content in the product decreases with an increase of the reactor inlet pressure.

Another non synthetic source for cyclohexane is natural gasoline and petroleum naphtha. However, only a small amount is obtained from this source. The 1994 U.S. production of cyclohexane was approximately 2.1 billion pounds (the 45th highest chemical volume).
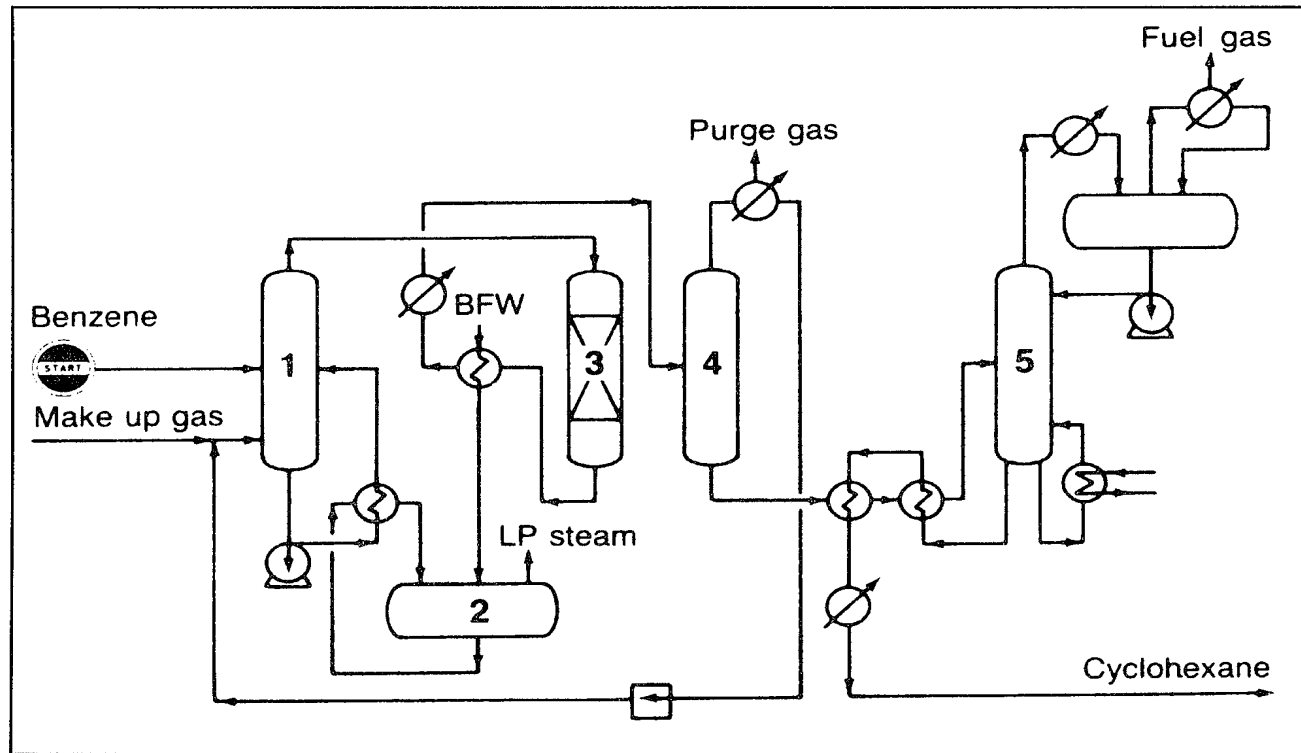
Figure 10-11. The Institu tFrancais du Petrole process for the hydrogenation of benzene to cyclohexane:(1) liquid-phase reactor, (2) heat exchanger, (3) catalytic pot (acts as a finishing reactor when conversion of the main reactor drops below the required level), (4) high-pressure separator,(5) stabilizer.
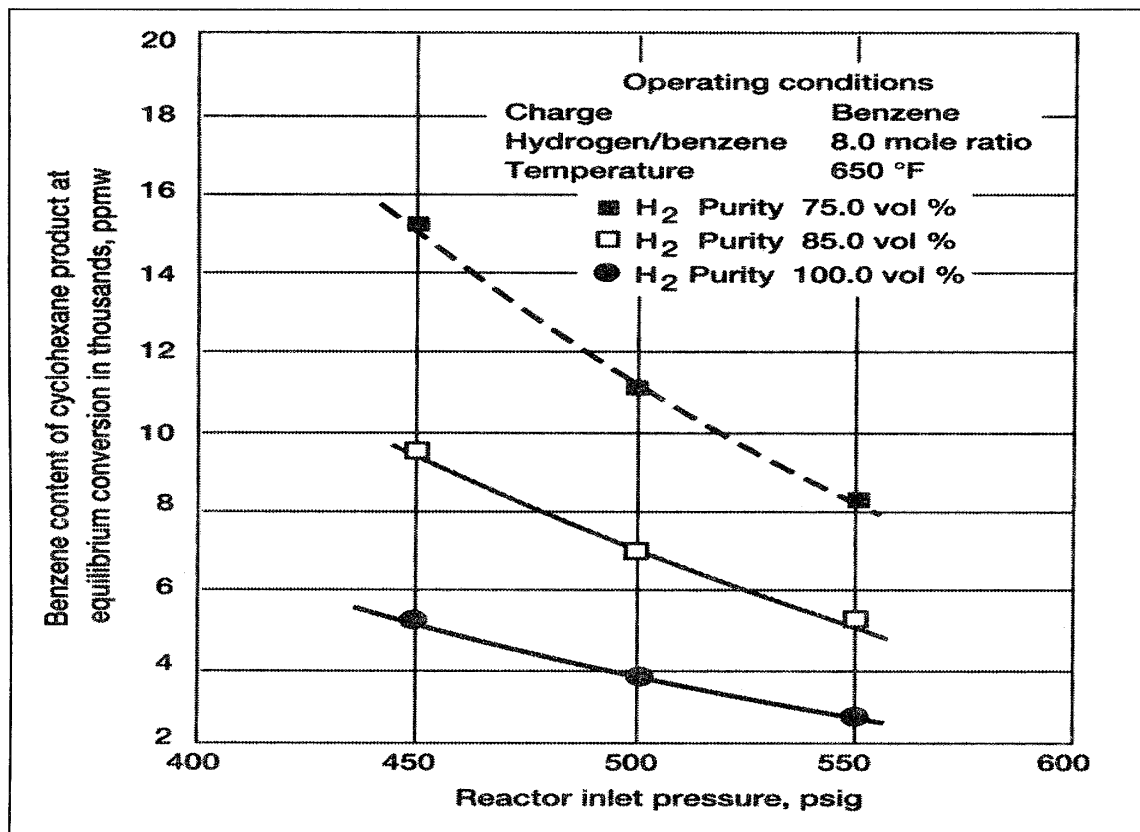
Figure 10-12. Effect of hydrogen purity and pressure on benzene conversion to cyclohexane.

Properties and Uses of Cyclohexane

Cyclohexane is a colorless liquid, insoluble in water but soluble in hydrocarbon solvents, alcohol, and acetone. As a cyclic paraffin, it can be easily dehydrogenated to benzene. The dehydrogenation of cyclohexane and its derivatives (present in naphthas) to aromatic hydrocarbons is an important reaction in the catalytic reforming process.

Essentia]ly, all cyclohexane is oxidized either to a cyclohexanone-cyclohexanol mixture used for making caprolactam or to adipic acid. These are monomers for making nylon 6 and nylon 6/6.

OXIDATION OF TOLUENE

Benzoic Acid
$$\left(\begin{array}{c} \text{COOH} \\ \bigcirc \end{array} \right)$$
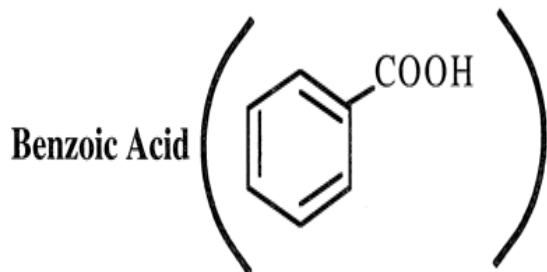
Oxidizing toluene in the liquid phase over a cobalt acetate catalyst produces benzoic acid. The reaction occurs at about 165°C and 10 atmospheres. The yield is over 90%:

$$\text{CH}_3\text{-}C_6H_5 + 1\tfrac{1}{2}O_2 \longrightarrow \text{COOH-}C_6H_5 + H_2O$$
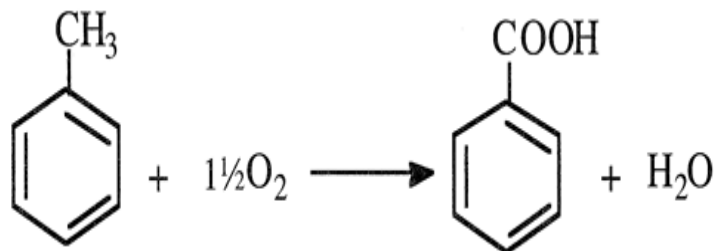
Benzoic acid (benzene carboxylic acid) is a white crystalline solid with a characteristic odor. It is slightly soluble in water and soluble in most common organic solvents.Though much benzoic acid gets used as a mordant in calico printing,it also serves to season tobacco, preserve food, make dentifrices, and killfungus. Furthermore it is a precursor for caprolactam, phenol, and terephthalic acid.

CHAPTER ELEVEN

Polymerization

INTRODUCTION

Polymerization is a reaction in which chain-like macromolecules are formed by combining small molecules (monomers).

Monomers are the building blocks of these large molecules called polymers. One natural polymer is cellulose (the most abundant organic compound on earth), a molecule made of many simple glucose units (monomers) joined together through a glycoside linkage. Proteins, the material of life, are polypeptides made of α-amino acids attached by an amide

$$-\left(\overset{\overset{\textstyle O}{\|}}{C}NH\right)-$$ linkage.

The polymer industry dates back to the 19th century, when natural polymers, such as cotton, were modified by chemical treatment to produce artificial silk (rayon). Work on synthetic polymers did not start until the beginning of the 20th century. In 1909, L. H. Baekeland prepared the first synthetic polymeric material using a condensation reaction between formaldehyde and phenol. Currently, these polymers serve as important thermosetting plastics (phenol formaldehyde resins). Since Baekeland's discovery, many polymers have been synthesized and marketed. Many modern commercial products (plastics, fibers, rubber) derive from polymers. The huge polymer market directly results from extensive work in synthetic organic compounds and catalysts. Ziegler's discovery of a coordination catalyst in the titanium family paved the road for synthesizing many stereoregular polymers with improved properties.
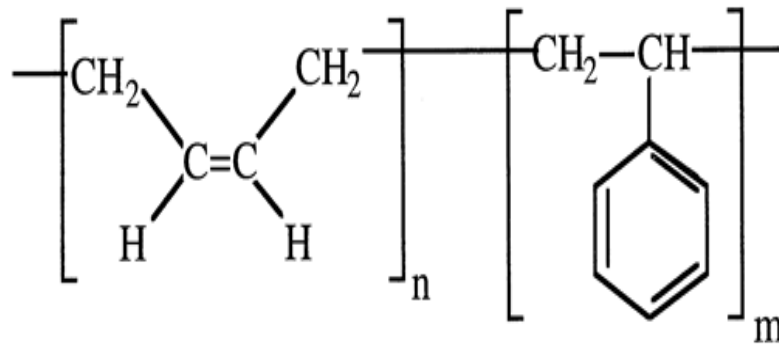
MONOMERS, POLYMERS, AND COPOLYMERS

A *monomer* is a reactive molecule that has at least one functional group (e.g. -OH, -COOH, $-NH_2$, -C=C-). Monomers may add to themselves as in the case of ethylene or may react with other monomers having different functionalities. A monomer initiated or catalyzed with a specific catalyst polymerizes and forms a macromolecule—a polymer. For example, ethylene polymerized in presence of a coordination catalyst produces a linear homopolymer (linear polyethylene):

$$n\ CH_2=CH_2 \longrightarrow [CH_2-CH]_n \qquad \text{(Linear polyethylene)}$$

A *copolymer,* on the other hand, results from two different monomers by addition polymerization. For example, a thermoplastic polymer with better properties than an ethylene homopolymer comes from copolymerizingn ethylene and propylene:

$$n\ CH_2=CH_2 + n\ CH_3CH=CH_2 \longrightarrow \left[CH_2CH_2\ CH_2\underset{\overset{|}{CH_3}}{CH} \right]_n$$
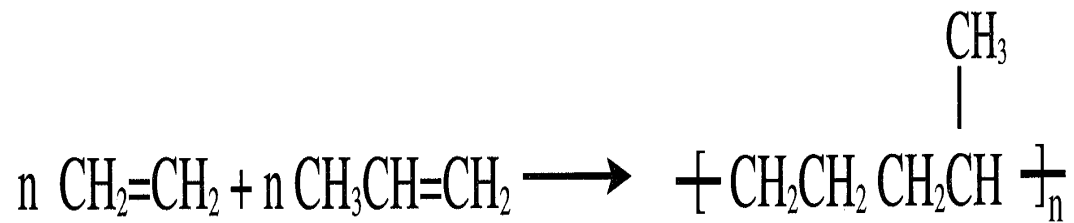
Block copolymers are formed by reacting two different *prepolymers,* which are obtained by polymerizing the molecules of each monomer separately. A block copolymer made of styrene and butadiene is an important synthetic rubber:

$$\left[\begin{array}{c} CH_2 \\ \\ \\ C=C \\ H \quad\quad H \end{array} CH_2 \right]_n \left[CH_2{-}CH \atop \hexagon \right]_m$$

Alternating copolymers have the monomers of one type alternating in a regular manner with the monomers of the other, regardless of the composition of the reactants. For example, an alternate copolymer of vinyl acetate and vinyl chloride could be represented as:

$$-CH_2CHCH_2CHCH_2CHCH_2CH-$$

with substituents OAC, Cl, OAC, Cl on successive CH groups.
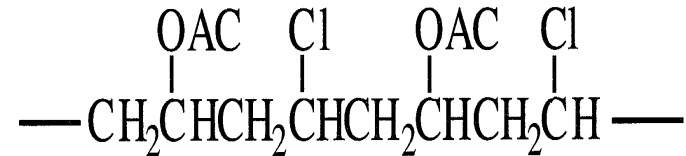
Random copolymers have the different monomer molecules distributed randomly along the polymer chain.

A polymer molecule may have just a linear chain or one or more branches protruding from the polymer backbone. Branching results mainly from chain transfer reactions and affects the polymer's physical and mechanical properties. Branched polyethylene usually has a few long branches and many more short branches

$$\sim CH_2-CH_2-CH-CH_2\sim$$
$$|$$
$$CH_2$$
$$|$$
$$CH_2$$
$$|$$
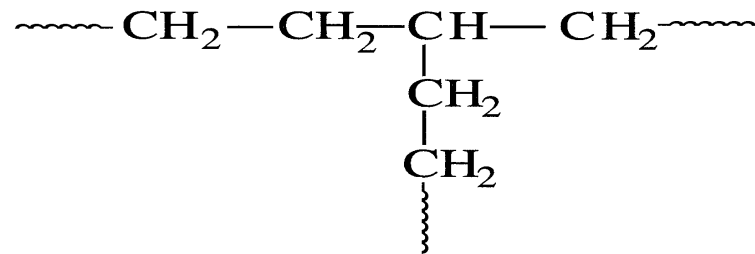
Intentional branching may improve the properties of the product polymer through grafting. A *graft copolymer* can be obtained by creating active sites on the polymer backbone. The addition of a different monomer then reacts at the active site and forms a branch. For example, polyethylene irradiated with gamma rays and then exposed to a reactive monomer, such as acrylonitrile, produces a polyethylene-polymer with acrylonitrile branches:

$$\sim\sim\!\!-CH_2\!\!-CH\!\!-CH_2\!\!-\sim\sim$$
$$|$$
$$CH_2$$
$$|$$
$$CHCN$$
$$|$$
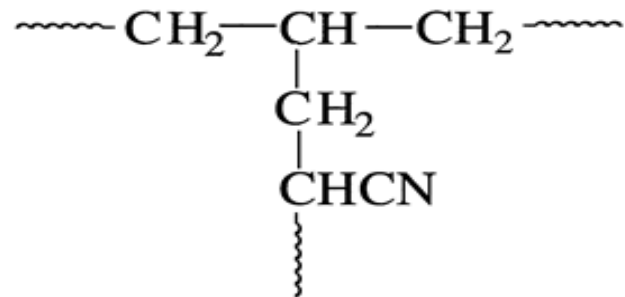
Crosslinked polymers have two or more polymer chains linked together at one or more points other than their ends. The network formed improves the mechanical and physical properties of the polymer.Crosslinking may occur during the polymerization reaction when multifunctional groups are present (as in phenol-formaldehyde resins) or through outside linking agents (as in the vulcanization of rubber with sulfur).