

# PLASTICS CHEMISTRY AND TECHNOLOGY

翻 印

華南工學院

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# PLASTICS CHEMISTRY AND TECHNOLOGY

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# 1

## Introduction

Polymers, the basis of plastics, have been around for a long time. Nature made polymers such as cellulose long before man invented synthetics. Cellulose is the primary constituent of wood fiber and cotton. Other natural polymers include proteins, natural rubber, tar, and resins.

Early man used natural polymers to form tools and weapons, but it was not until the late nineteenth century that man started modifying polymers to create plastics, which were first made by modifying natural polymeric materials. Nitrocellulose was the first major plastic commercialized. In its natural state, cellulose will not melt and is insoluble. Nitrating makes it both soluble and heat-formable. In 1870, John W. and I. S. Hyatt introduced a plastic known as Celluloid.<sup>1</sup> This clear, tough, moldable material was made from nitrocellulose plasticized with camphor. Celluloid was widely used for common items such as brushes, combs, photographic film, glue, fibers, lacquers, and automobile safety glass.

Totally synthetic plastics were first introduced in 1908. Dr. Leo Baekeland developed phenolic and marketed it under the trade name Bakelite.<sup>2</sup> This became the standard plastic for telephone receivers, electrical insulators, and cooking utensil handles. Plastics became significant materials even though the chemistry was not well understood. The concept of polymers was not fully accepted until the 1920's.

The field of plastics proliferated after the chemistry of polymerization became known. Some of the most significant plastics are listed with their approximate commercialization dates.<sup>1,2,3,4,5</sup>



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- 1870 Celluloid (nitrocellulose)
- 1908 Bakelite (phenolic)
- 1919 Vinyl acetate
- 1927 Cellulose acetate
- 1928 Ureas
- 1931 Acrylics
- 1936 Polyvinyl chloride (PVC)
- 1938 Cellulose acetate butyrate
- 1938 Polyamides (nylon)
- 1938 Polystyrene
- 1939 Melamines
- 1939 Polyvinylidene chloride
- 1942 Polyethylene
- 1942 Polyesters
- 1943 Silicones
- 1943 Teflon
- 1947 Epoxy
- 1948 Acrylonitrile-butadiene-styrene (ABS)
- 1948 Polychlorotrifluoroethylene (Kel-F)
- 1953 Polyurethanes
- 1957 Polypropylene
- 1958 Acetals
- 1959 Polycarbonate
- 1964 Polyphenylene oxide
- 1964 Polyimide
- 1965 Polysulfone
- 1965 Polymethyl pentene (TPX)
- 1969 Polybutylene terephthalate polyester (PBT)
- 1973 Polybutylene

Since 1950, the list has expanded at an accelerated rate, producing increased temperature capability and tougher material.

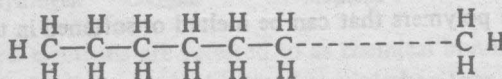
### What is a Polymer?

A polymer is simply a very large molecule formed by joining many small molecules known as monomers. As the size of a molecule changes, so do the properties. These variations can be observed in Table 1-1.

Table 1-1. Effect of Chain Length on Properties of Carbon Compounds.

NUMBER OF CARBON ATOMS	NAME	FORM
1	Methane	Gas
2	Ethane	Gas
3	Propane	Gas
7	Heptane	Liquid
12-14	Oil	Viscous liquid
26-50	Wax	Weak solid
1,000	Low molecular weight polyethylene	Flexible solid
3,000-350,000	High molecular weight polyethylene	Stiff, strong solid

All the above compounds are straight chain carbon hydrogen molecules.



The basic difference is the length of the chains. Melting point and strength are both proportional to the size of the molecules.

## REFERENCES

1. Billmeyer, F. W., *Textbook of Polymer Science*, John Wiley & Sons, New York, 1971 (pp. 12-14).
2. Simonds, H. R. and Church, J. M., *A Concise Guide to Plastics*, Van Nostrand Reinhold, New York, 1963 (p. 2).
3. Walton, R. K., "Polysulfone Resin," *Modern Plastics Encyclopedia*, McGraw-Hill, New York, 1968 (p. 284).
4. Kendall, V. G., "Polymethylpentene," *Modern Plastics Encyclopedia*, 1972-1973, McGraw-Hill, New York, 1972 (p. 88).
5. "1976 Facts and Figures on the Plastics Industry," Society of Plastics Industry New York, 1976.

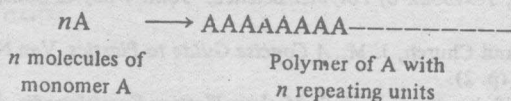
# 2

## Thermoplastic Polymers

Thermoplastics are polymers that can be melted or softened in the polymerized form.

### POLYMERIZATION CONCEPTS

Polymers are formed by reacting small molecules (monomers) together. In some cases the molecules will react with themselves to form homopolymers. Others require two different monomers that are reactive with each other. In all cases the monomers react in a succession of reactions to form a large molecule.



### Polymer Size

Molecular weight is customarily used to represent the molecular size. Thus, if a polymer of ethylene contained 1,000 molecules of ethylene per molecule, the polymer's molecular weight can be computed as shown below.

$$28 \times 1,000 = 28,000$$

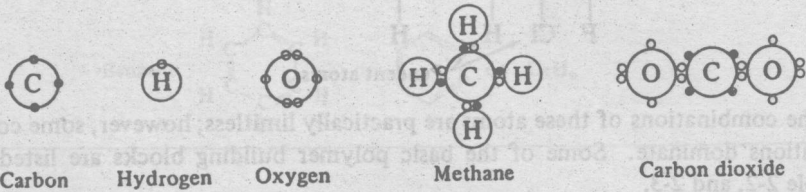
MW of ethylene
repeating units
MW of polymer

The process of polymerization is random, therefore some molecules grow much larger than others. Plastics are a mixture of different size molecules. Molecular size is expressed as average molecular weight.

## Building Blocks

Most polymers are made up of carbon, hydrogen, oxygen, and nitrogen; however, increasing use is being made of silicon, chlorine, fluorine, bromine, phosphorus, and sulfur.

The electron shells of each atom determine its valence or bonding capability. The outer shell of electrons will seek a level of 8, except for hydrogen, which is satisfied with 2. This condition is known as a balanced electron count. Electrons are shared between atoms to accomplish the balance of 8 or 2 as shown in the following examples.



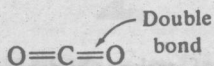
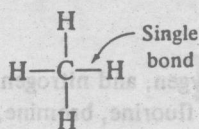
Pairs of shared electrons are referred to as chemical bonds. These are shown diagrammatically by lines. A double bond results when four electrons are shared. Similarly, a triple bond can be formed with six shared electrons.

Table 2-1. Properties of Elements Used in Polymers.

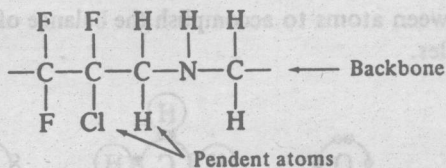
ATOM	SYMBOL	VALENCE IN POLYMERS	MW	COMMENTS
Carbon	$\begin{array}{c}   \\ -C- \\   \end{array}$	4	12	Chain formers
Silicon	$\begin{array}{c}   \\ -Si- \\   \end{array}$	4	28	
Nitrogen	$\begin{array}{c}   \\ -N- \\   \end{array}$	3	14	
Oxygen	$\begin{array}{c}   \\ -O- \\   \end{array}$	2	16	
Sulfur	$\begin{array}{c}    \\ -S- \\    \end{array}$	2,4,6	32	
Phosphorus	$\begin{array}{c}    \\ -P- \\   \end{array}$	3,5	31	Pendent atoms
Hydrogen	H—	1	1	
Chlorine	Cl—	1	35.5	
Fluorine	F—	1	19	
Bromine	Br—	1	80	



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Atoms with multiple bond capability can be used in forming the backbone of polymer chains. Atoms with single bond capability are limited to pendent side positions.



The combinations of these atoms are practically limitless; however, some combinations dominate. Some of the basic polymer building blocks are listed in Table 2-2, and 2-3.

The compounds in Table 2-2 are referred to as unsaturated compounds. They all have double bonds between carbon atoms capable of accepting additional hydrogen. It should be noted that the unsaturated compounds all end in "ene."

Saturated compounds (see Table 2-3) have all available sites occupied and therefore have no double bonds. These compounds have names ending with "ane."

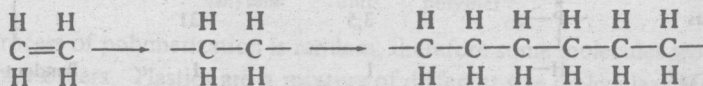
### POLYMERIZATION MECHANISMS

Mechanisms by which polymerization takes place fall into two general categories—addition and condensation.

#### Addition Polymerization<sup>1,2</sup>

Addition polymerization is the combination of monomers by reaction of carbon carbon double bonds ( $\text{C}=\text{C}$ ). Most of the addition reactions are of the ethylene type.

An ethylene double bond will open up when exposed to an appropriate initiator. A series of reactions follow, resulting in a long chain molecule.



A common type of initiator is the free radical, which is a compound with an unpaired electron. For example, oxygen normally has two bonds, while compounds can be formed with only one.

Table 2-2. Unsaturated Double Bond Compounds.


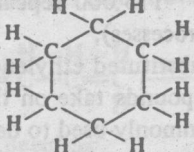

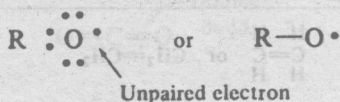
Ethylene	$\begin{array}{c} \text{H} \quad \text{H} \\ \text{C}=\text{C} \\ \text{H} \quad \text{H} \end{array}$ or $\text{CH}_2=\text{CH}_2$
Propylene	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \text{C}=\text{C}-\text{C} \quad \text{H} \\ \text{H} \quad \quad \text{H} \end{array}$ or $\text{CH}_2=\text{CH}-\text{CH}_3$
Butadiene	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \text{C}=\text{C}-\text{C}=\text{C} \\ \text{H} \quad \quad \text{H} \end{array}$ or $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
Benzene	$\begin{array}{c} \text{H} \\ \text{C} \\ \text{H} \quad \text{C} \quad \text{H} \\ \text{H} \quad \text{C} \quad \text{H} \\ \text{H} \quad \text{C} \quad \text{H} \\ \text{H} \end{array}$ or  or $\text{C}_6\text{H}_6$

Table 2-3. Saturated Single Bond Compounds.

Methane	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$ or $\text{CH}_4$
Ethane	$\begin{array}{c} \text{H} \quad \text{H} \\ \text{H} \text{C}-\text{C} \text{H} \\ \text{H} \quad \text{H} \end{array}$ or $\text{CH}_3-\text{CH}_3$
Propane	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \text{H} \text{C}-\text{C}-\text{C} \text{H} \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$ or $\text{CH}_3-\text{CH}_2-\text{CH}_3$
Butane	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \text{H} \text{C}-\text{C}-\text{C}-\text{C} \text{H} \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$ or $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$
Isobutane	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \text{H} \text{C}-\text{C} \quad \text{H} \\ \text{H} \quad \quad \text{H} \end{array}$ or $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3-\text{CH} \\ \text{CH}_3 \end{array}$
Cyclohexane	 or  or $\text{C}_6\text{H}_{12}$

Note: S in a ring indicates saturation.

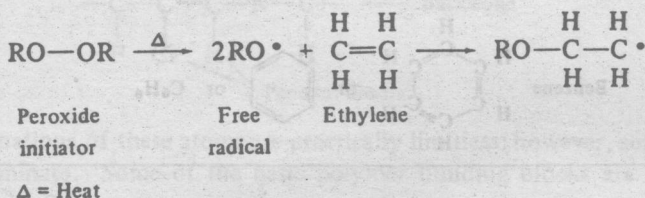
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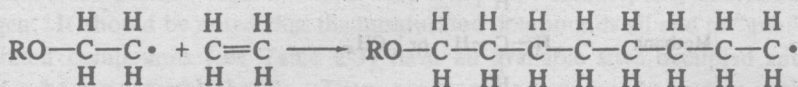
Free radical, where R indicates any chemical group.

Such a compound can be formed by breaking a peroxide bond ( $-\text{O}-\text{O}-$ ). The sequence of events from start of activation to finished polymer are shown below.

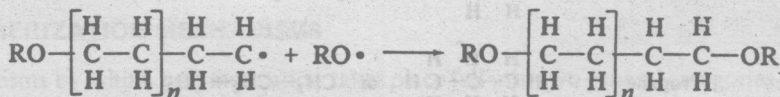
### 1. Initiation



### 2. Propagation



### 3. Termination




**Note:** The brackets indicate repeating units where  $n$  = the number of repeating units.

Addition polymerization continues to propagate until something terminates it. Another free radical can terminate the reactivity or two growing chains can react together. Trace amounts of contamination can also terminate polymer chains, resulting in low molecular weight.

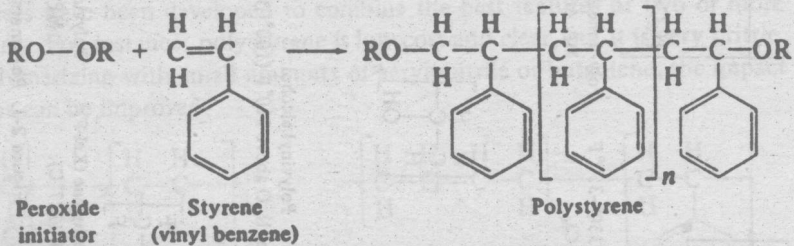
Useful plastics are obtained when the average polyethylene chain length reaches 700 repeating ( $\text{C}-\text{C}$ ). Strength and hardness increases with larger molecules. Polyethylene is produced with up to  $\sim 175,000$  repeating units by employing special catalysts (Ziegler and Phillips processes).

**Vinyl and Vinylidene Polymers.** Substituted ethylene monomers are used to achieve various properties. The compounds take on the form shown in Table 2-4. It may be noted that vinyl is commonly used to denote polyvinyl chloride. Chemically, it refers to ethylene compounds with one substitution. Vinylidene compounds have two substitutions on the same carbon atom.

Table 2-4. Vinyl Type Monomers.

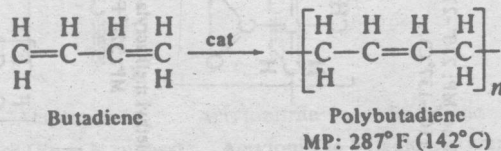
$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{C}=\text{C} \\   \quad   \\ \text{H} \quad \text{R} \end{array}$ <p>Vinyl monomer</p>	Ethylene	R	
	Vinyl chloride	—H	
	Propylene	—Cl	
		—CH <sub>3</sub>	
	Vinyl acetate	$-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	
$\begin{array}{c} \text{H} \quad \text{R}'' \\   \quad   \\ \text{C}=\text{C} \\   \quad   \\ \text{H} \quad \text{R}' \end{array}$ <p>Vinylidene monomer</p>	Styrene (vinyl benzene)		
		R'	R''
	Isobutylene	—CH <sub>3</sub>	—CH <sub>3</sub>
	Vinylidene chloride	—Cl	—Cl
	Methyl methacrylate	—CH <sub>3</sub>	$-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_3$

Addition reactions can be carried out readily with substituted ethylene compounds, such as styrene.



Some of the polymers formed this way are given in Figure 2-1. The polymers in Figure 2-1 all have straight carbon backbones, but properties vary widely with different side groups. Properties of materials will be discussed in subsequent chapters.

**Polydienes.** Butadiene polymerization is similar to vinyl polymerizations, except that a reactive double bond remains after the initial polymerization. This process will be discussed further in Chapter 3.



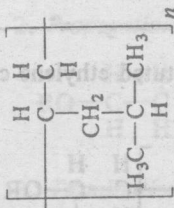




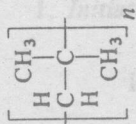
Polyethylene: MP: 230°-278° F  
(110°-137° C).



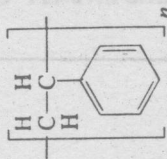
Polypropylene: MP: 330°-350° F  
(165°-177° C).



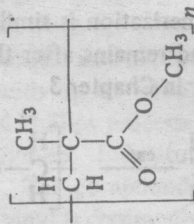
Poly-4-methylpentene (TPX):  
MP: 464° F (240° C).



Polyisobutylene (Vistanex):  
MP: depends on MW.



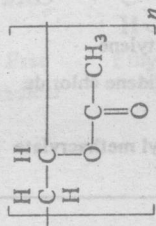
Polystyrene: MP: 330°-470° F  
(150°-243° C).



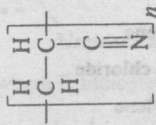
Polymethyl methacrylate (Plexiglass, Lucite):  
MP: 320° F (160° C).



Polyvinyl alcohol:  
loses H<sub>2</sub>O above 210° F (100° C).



Polyvinyl acetate (white glue):  
MP: 350° F (177° C).



Polyacrylonitrile (Orlon): does not melt  
(see Chapter 4).



Polytetrafluoroethylene (TFE Teflon):  
softens at 700° F (370° C).



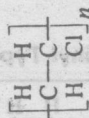
Chlorotrifluoroethylene (Kel-F):  
MP: 440° F (227° C).



Polyvinyl fluoride (Tedlar):  
MP: 400° F (204° C).



Polyvinylidene chloride (Saran):  
MP: 350° F (177° C).

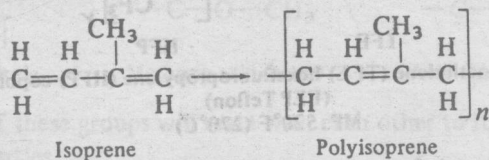


Polyvinyl chloride (PVC):  
MP: ~400° F (~204° C).

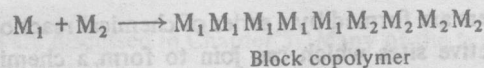
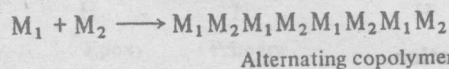
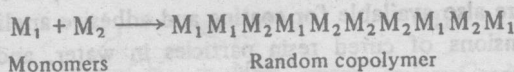
Figure 2-1. Polymers Based on the Ethylene Chain.

Butadiene is used to form both rigid plastics and butyl rubber.

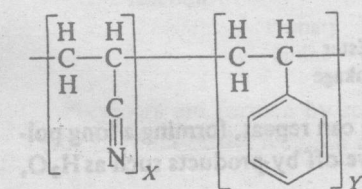
Isoprene polymerizes by the same mechanism and is also used in rubber. Natural rubber is primarily polyisoprene.



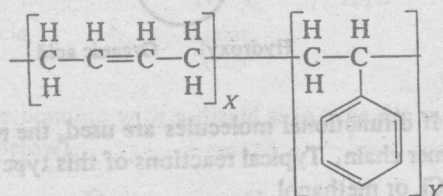
**Copolymers.** Mixtures of two or more types of monomers can be polymerized to form copolymers. The polymer can have a random mixture or an orderly arrangement of the different monomers.



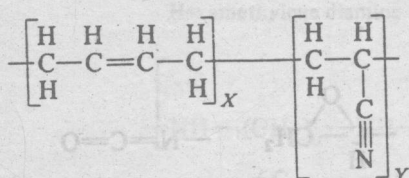
Each type of polymer has different properties. Many types of copolymers and terpolymers have been developed to combine the best features of two or more monomers. For instance, polystyrene is low cost and clear, but it is very brittle. By copolymerizing with small amounts of acrylonitrile or butadiene, the impact properties can be improved.



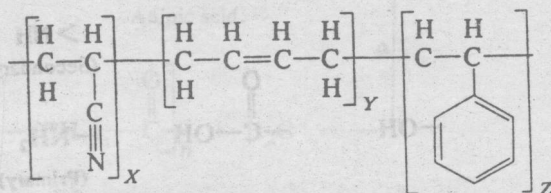
Acrylonitrile Styrene  
Acrylonitrile-styrene copolymer (SAN)



Butadiene Styrene  
Butadiene-styrene copolymer (Buna-S rubber)

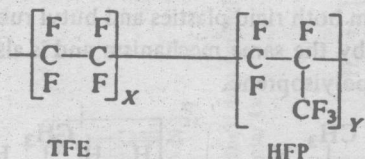


Butadiene Acrylonitrile



Acrylonitrile Butadiene Styrene

Butadiene-acrylonitrile copolymer (Buna-N rubber) Acrylonitrile-butadiene-styrene terpolymer (ABS)

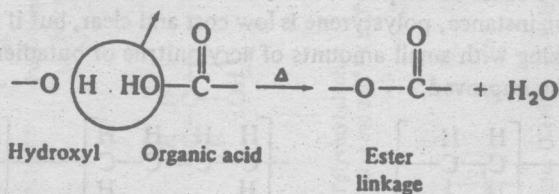


Tetrafluoroethylene (TFE)-hexafluoropropylene (HFP) copolymer  
(FEP Teflon)  
MP: 520°F (270°C)

Addition polymers are the most widely used today. Polyvinyl chloride, polyethylene, and styrene based polymers account for much of the volume. The majority of addition polymers are polymerized by the resin manufacturer. The plastics are then melted or dissolved for molded, extruded, or coated products. Polymer latexes are also available for coating and adhesive applications. These latexes are suspensions of cured resin particles in water, and are discussed later in this chapter.

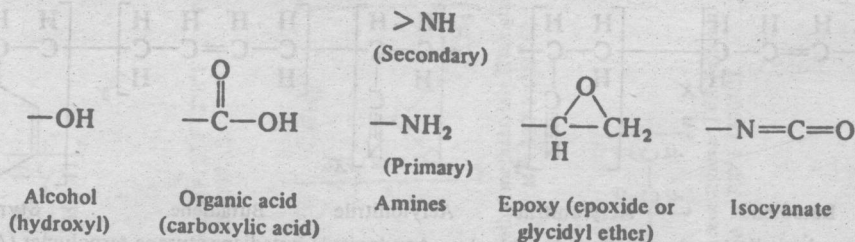
### Condensation Polymerization

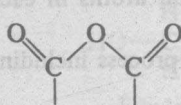
Condensation polymers are formed by a series of chemical reactions. These reactions involve two active sites which can join to form a chemical bond. By-products are given off by many of these reactions. Two reactive molecules can join to form a new compound plus a by-product, as shown below.



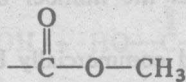
If difunctional molecules are used, the reaction can repeat, forming a long polymer chain. Typical reactions of this type will give off by-products such as H<sub>2</sub>O, HCl, or methanol.

Many compounds exist that will react together. Some of the reactive groups commonly used to form condensation polymers are shown.

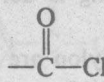




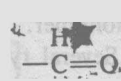
Acid anhydride



Methoxy acid (ester)



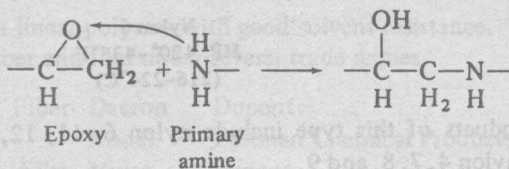
Acid chloride



Aldehyde

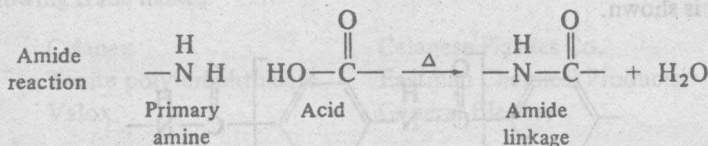
A number of these groups will react with each other to form polymers with very diverse properties.

Several reactions have been devised that do not liberate any by-products. These are useful for potting and other applications where by-products would degrade the product. The epoxy reaction is a good example of such a system.

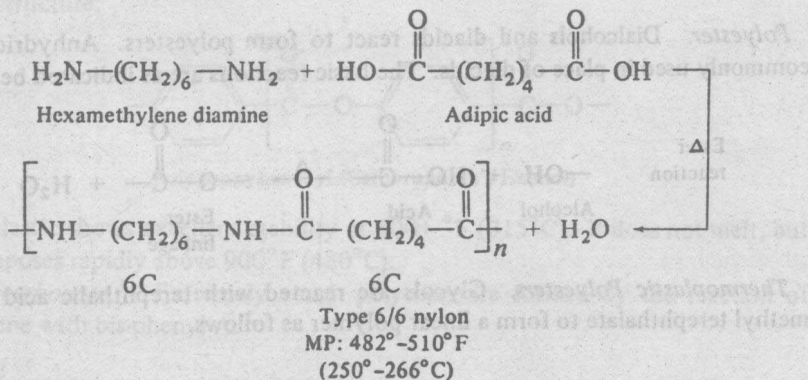


Epoxy resins are discussed in Chapter 5. Many of the typical condensation polymers are discussed below.

**Polyamides (Nylon).** Amides are condensation products of an amine and carboxylic acid. The reaction is shown below.



Polymers are formed by reacting a diamine with a diacid as in type 6/6 nylon (the product of the reaction shown below).



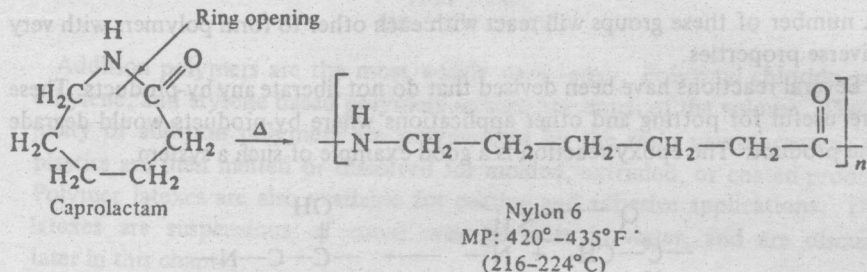


## 14 PLASTIC CHEMISTRY AND TECHNOLOGY

**Note:** The numbering is derived from the number of carbon atoms in each monomer.

Several types of nylon are produced commercially by this process including 6/6, 6/9, 6/10, and 6/12.

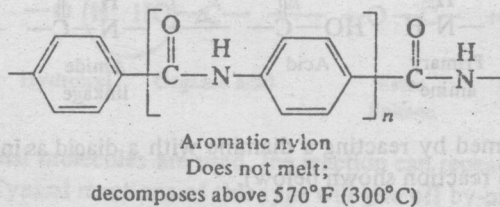
A ring opening reaction is used to form nylon 6.<sup>4</sup>



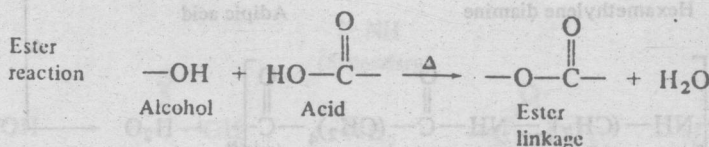
Commercial products of this type include nylon 6, 11, 12, and—in limited commercial use—nylon 4, 7, 8, and 9.

Nylon 6 and 6/6 are used extensively in tire cord, moldings, and fabrics. Higher numbered nylons have lower moisture absorption and higher flexibility.

**Aromatic Polyamide.**<sup>2,5</sup> Rings in the polymer chain increase the thermal stability. Polymers of this type are available in fiber and paper form from Dupont under the trade names Aromid, Nomex, and Kevlar. The general form of these polymers is shown.



**Polyester.** Dialcohols and diacids react to form polyesters. Anhydrides are commonly used in place of diacids. The basic reactions are as indicated below.



**Thermoplastic Polyesters.** Glycols are reacted with terephthalic acid or dimethyl terephthalate to form a linear polymer as follows.