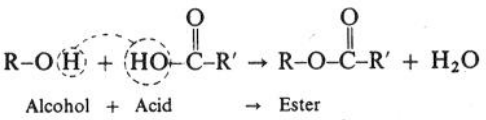
Natural r[illegible]'s a classic example of these two categories. Introduced to Europe by Columbus, natural rubber did not achieve commercial significance for centuries; because it was a thermoplastic, articles made of it would become soft and sticky on hot days. In 1839, Charles Goodyear discovered the curing reaction with sulfur (which he called *vulcanization* in honor of the Roman god of fire) that converted the polymer to a thermoset. This allowed the rubber to maintain its useful properties to much higher temperatures, which ultimately led to its great commercial importance.

2.2 CHEMISTRY OF SYNTHESIS

Pioneering workers in the field of polymer chemistry soon observed that they could produce polymers by two familiar types of organic reactions.

A Condensation

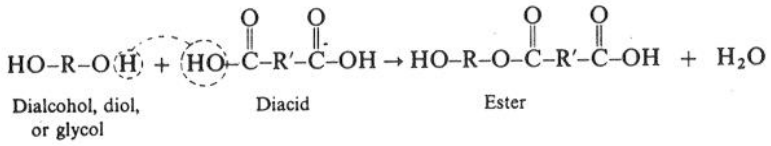
Polymers formed from a typical organic condensation reaction, in which a small molecule (most often water) is split out, are known, logically enough, as *condensation polymers*. The common esterification reaction of an organic acid and an organic base (alcohol) illustrates the simple "lasso chemistry" involved:



The –OH group on the alcohol and the $HO-\overset{O}{\overset{\|}{C}}-$ on the acid are known as *functional groups*, those parts of a molecule that participate in a reaction. Of course, the ester formed in the preceding reaction is not a polymer because we have only hooked up two small molecules, and the reaction is finished far short of anything that might be considered "many membered."

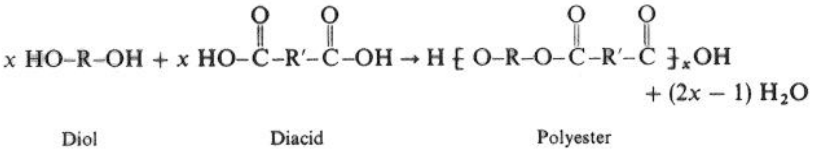
At this point it is useful to introduce the concept of functionality. Functionality is the number of bonds a mer can form with other mers in a reaction. In condensation polymerization, it is equal to the number of functional groups on the mer.

It is obvious from the example above that each of the reactants is monofunctional, and that reactions between monofunctional mers cannot lead to polymers. But now consider what happens if each reactant is difunctional, allowing it to react at each end:



The resulting product molecule is still difunctional. Its left end can react another diacid molecule and its right end with another molecule of diol, and after each subsequent reaction, the growing molecule is still difunctional and capable of undergoing further growth, leading to a true polymer molecule.

In general, the *polycondensation* of x molecules of a diol with x molecules of a diacid to give a *polyester* molecule is written as

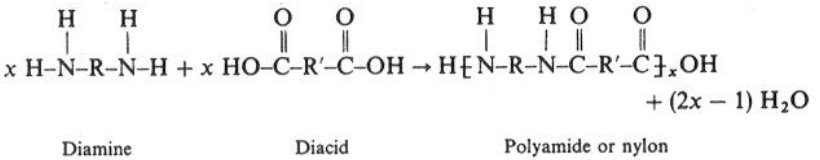


In the polyester molecule above, the structure in brackets is the repeating unit, and is what distinguishes one polymer from another, while the $\{O-\overset{O}{\overset{\|}{C}}\}$ linkage characterizes all polyesters. The generalized organic groups R and R' may vary widely (with a consequent variation in the properties of the polymer), but as long as the repeating unit contains the $\{O-\overset{O}{\overset{\|}{C}}\}$ linkage, the polymer is a polyester.

The quantity x is the *degree of polymerization*, the number of repeating units strung together like identical beads in the polymer chain. It is sometimes also called the *chain length*, but it is a pure number, not a length.

The nomenclature above was introduced by Wallace Hume Carothers, who, with his group at Du Pont, invented neoprene and nylon in the 1930s, and was one of the founders of modern polymer science.[1]

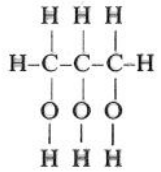
Another functional group that is capable of taking part in a condensation is the amine ($-NH_2$) group, *one* hydrogen of which reacts with a carboxylic acid group in a manner similar to the alcoholic hydrogen to form a polyamide or nylon:



The $\{-\overset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-\}$ linkage characterizes nylons. (Both amine hydrogens can react with two acid groups which are on adjacent carbon atoms in a benzene ring. This gives a polyimide linkage, and is illustrated in Example 4R at the end of the chapter.) The examples above serve to illustrate that reactants must be at least difunctional if a polymer is to be obtained. Molecules with higher degrees of

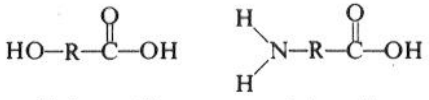
Fundamental Principles of Polymeric Materials by. Stephen L. Rosen, 2nd Ed. (1993)

functionality will also lead to polymers. For example, glycerine



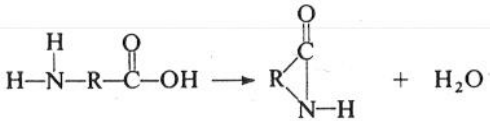
is trifunctional in a polyesterification reaction.

It is also possible to form condensation polymers from a single monomer that contains the two complementary reactive groups in the same molecule, for example,



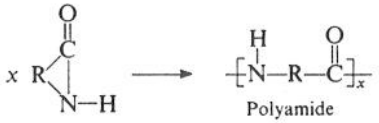
Hydroxy acid Amino acid

In principle, the hydroxy acid can condense directly to form a polyester and the amino acid a polyamide (proteins are poly amino acids). The reactions do not always proceed in a straightforward fashion, however. If R is large enough, say three carbon atoms or more, the difunctional monomers above may "bite their own tails," condensing to form a cyclic structure:



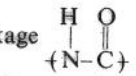
Amino acid Lactam

This cyclic compound can then undergo a *ring-scission* polymerization, in which the polymer is formed without splitting out a small molecule, because the small molecule had been eliminated previously in the cyclization step:



Polyamide

Despite the lack of elimination of a small molecule in the actual polymerization step, the products can be thought of as having been formed by a direct condensation from the monomer, and are usually considered condensation polymers.

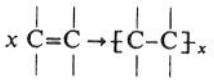
Note that the characteristic nylon linkage  is split up, and not immediately obvious in the repeating unit as written above. If you place a second repeating next to the one shown, it becomes evident. This illustrates the somewhat arbitrary location of the brackets, which should not obscure the fact that the polymer is a nylon.

B Addition

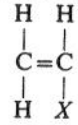
The second polymer-formation reaction is known as addition polymerization and its products as *addition polymers.* Addition polymerizations have two distinct characteristics:

1. No molecule is split out; hence, the repeating unit has the same chemical formula as the monomer.
2. The polymerization reaction involves the opening of a double bond.*

Monomers of the general type undergo addition polymerization:

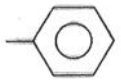


The double bond "opens up," forming bonds to other monomers at each end, so *a double bond is difunctional* according to our general definition of functionality. The question of what happens at the ends of the polymer molecule will be deferred for a discussion of polymerization mechanisms in Chapter 10.

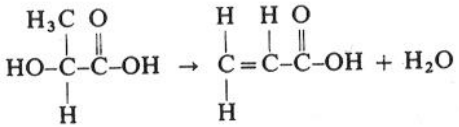
An important subclass of the double-bond containing monomers is the vinyl monomers,  . Addition polymerization is occasionally referred to as vinyl polymerization. Table 2.1 lists some commercially important vinyl monomers.

* Although aromatic rings are often symbolized by , this is a poor representation of resonance-stabilized structures, which are completely inert to addition polymerization. They are more properly symbolized by to avoid confusion with the ordinary double bond. To save space, we will sometimes also use ϕ to represent the phenyl ring.

Table 2.1 Some Commercially Important Vinyl Monomers

Monomer	$-X$
Ethylene	$-H$
Styrene	
Vinyl chloride	$-Cl$
Propylene	$-CH_3$
Acrylonitrile	$-C\equiv N$

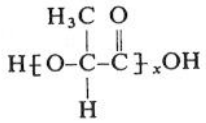
Example 1. Lactic acid can be dehydrated to acrylic acid according to the following reaction:



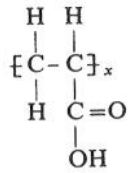
Lactic acid Acrylic acid

Each acid forms a polymer. Write the structural formulae for the repeating unit of the polymer formed from each acid.

Solution. Lactic acid is an hydroxy acid, and will undergo condensation polymerization, splitting out water from the –OH and $-\overset{O}{\overset{\|}{C}}-OH$ groups to give a polyester:

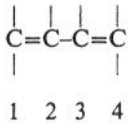


Note again that in the above formula, the characteristic polyester linkage $\{O-\overset{O}{\overset{\|}{C}}\}$ is split up. Acrylic acid is a vinyl monomer, and will undergo addition polymerization to give

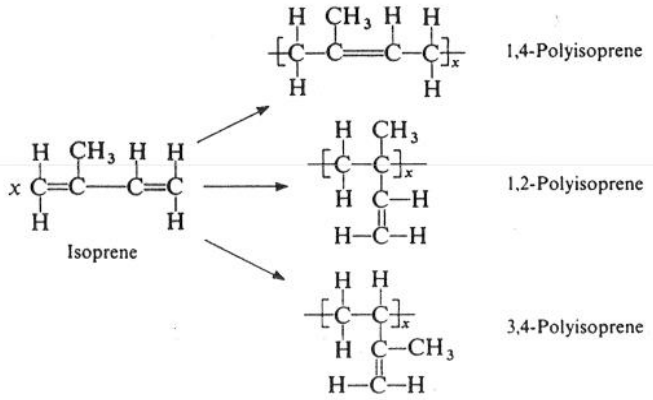


Interestingly, the ester linkage in poly(lactic acid) is easily hydrolyzed giving down the polymer. This for many years prevented commercial application of the polymer. Now, however, there is great interest in this polymer as a biodegradable plastic.

Dienes (the carbon atoms in which are numbered from one end)



also undergo addition polymerization. Addition polymerization of a diene "uses up" one of the two double bonds per monomer, giving an *unsaturated* polymer, that is, one that contains double bonds. In this case, there is one double bond per repeating unit. Furthermore, diene polymerization can lead to several *structural isomers* in the polymer. If the monomer is symmetrical with regard to substituent groups, it can undergo 1, 2 addition and 1, 4 addition. If unsymmetrical, there is the added possibility of 3, 4 addition. (For symmetrical dienes, the 1, 2 and 3, 4 reactions are the same.) This is illustrated below for the addition polymerization of isoprene (2-methyl-1,3-butadiene):



The 1, 2 and 3, 4 reactions are sometimes known as *vinyl* addition, because part of the diene monomer simply acts as an X group in a vinyl monomer.

2.3 STRUCTURE

As an appreciation for the molecular structure of polymers was gained, three major structural categories emerged. These are illustrated schematically in Fig. 2.1.

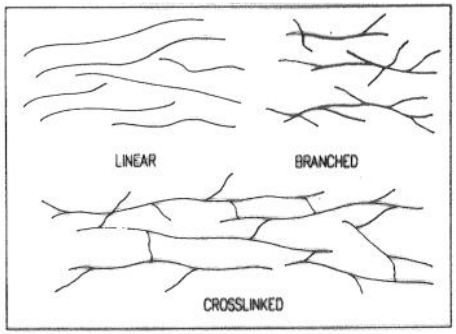


Figure 2.1 Schematic diagram of polymer structures.

A Linear

If a polymer is built from strictly difunctional monomers, the result is a *linear* polymer chain. A scale model of a typical linear polymer molecule made from 0.5-cm-diameter clothesline would be about three meters long. This isn't a bad analogy: The chains are long, flexible, essentially one-dimensional structures. The term linear can be somewhat misleading, however, because the molecules don't necessarily assume a geometrically linear conformation.

Random Copolymers

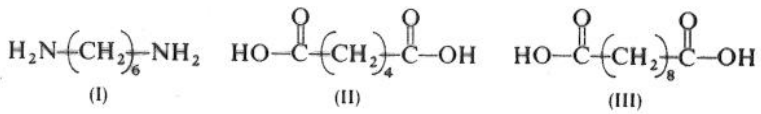
Polymers consisting of chains that contain a single repeating unit are known as *homopolymers*. If, however, the chains contain a random arrangement of two separate and distinct repeating units, the polymer is known as a *random* or *statistical copolymer*, or just plain *copolymer*. A random copolymer might be formed by the addition polymerization of a mixture of two different vinyl monomers, A and B (the degree of "randomness" depends on the relative amounts and reactivities of A and B, as we shall see later), and be represented as

AABAAABBABAAB

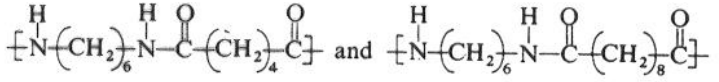
and called poly(A-*co*-B), where the first repeating unit listed is the one present in the greater amount. For example, a random synthetic rubber copolymer of 75% butadiene and 25% styrene would be termed poly(butadiene-*co*-styrene). Of course, ter- and higher multipolymers are possible.

It must be emphasized that the products of condensation polymerizations that require two different monomers to provide the necessary functional groups, for example, a diacid and a diamine, are not copolymers, because they contain only one repeating unit. If, however, two different diamines were to be used, leading to two distinct repeating units, the product would be a copolymer.

Example 2. Illustrate the repeating units that result when three [illegible] of hexamethylene diamine (I) are condensed with two moles of adipic acid (II) and one mole of sebacic acid (III), and name the resulting copolymer:



Solution. The two repeating units are



The formal (if unwieldly) name for the copolymer containing these two repeating units is poly(hexamethylene adipamide-*co*-hexamethylene sebacamide).

Block Copolymers

Under certain conditions, linear chains can be formed that contain long contiguous blocks of two (or more) repeating units combined in the chains, a block copolymer:

AAAAAAAAAAAAAAAAAAAAABBBBBBBBBBBBBBBBBB

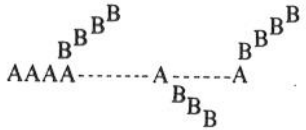
Such a polymer would be termed poly(A–*b*–B).

B Branched

If a few points of tri (or higher) functionality are introduced (either intentionally or through side reactions) at random points along linear chains, *branched* molecules result. Branching can have a tremendous influence on the properties of polymers through steric (geometric) effects.

Graft copolymers

Under specialized conditions, branches of repeating unit B may be "grafted" to a backbone of linear A. This structure is known as a *graft copolymer*:



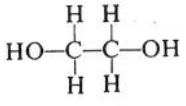
The graft polymer above would be called poly(A–*g*–B), the backbone repeating unit being the one listed first.

C Crosslinked or Network

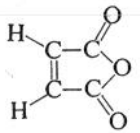
As the length and frequency of the branches on polymer chains increases, the probability that the branches will finally reach from chain to chain, connecting them together, becomes greater. When all the chains are finally connected together in three dimensions by these crosslinks, the entire polymer mass becomes one tremendous molecule, a *crosslinked* or *network* polymer. In a truly crosslinked polymer mass, all the atoms are connected to one another by covalent bonds. The polymer in a bowling ball, for example, has a molecular weight on the order of 10^{27} g/mol. Remember this the next time someone suggests that individual molecules are too small to be seen with the naked eye.

Crosslinked or network polymers may be formed in two ways: (1) by starting with reaction masses containing sufficient amounts of tri- or higher-functional monomer, or (2) by chemically creating crosslinks between previously formed linear or branched molecules ("curing"). The latter is precisely what vulcanization does to natural rubber, and this fact serves to introduce the connection between the phenomenological "reaction to temperature" classification and the more fundamental concept of molecular structure. This important connection will be clarified through a discussion of bonding in polymers.

Example 3. Show (*a*) how a linear, unsaturated polyester is produced from ethylene glycol (I) and maleic anhydride (II), and (*b*) how the linear, unsaturated polyester is crosslinked with a vinyl monomer such as styrene.

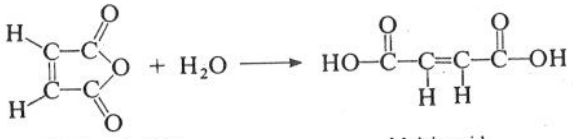


(I)



(II)

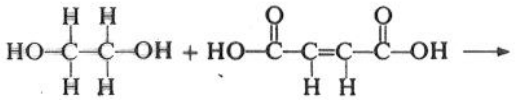
Solution. First, realize that an acid anhydride is simply a diacid with a mole of water split out from the two acid groups. (This is the only common example of acid groups condensing with one another. You can't ordinarily form polymers this way). When considering the reaction of an acid anhydride, (conceptually) hydrate it back to the diacid:

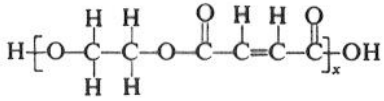


Maleic anhydride

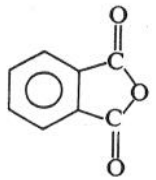
Maleic acid

Then condense the diacid with the diol to form a polyester with one double bond per repeating unit:





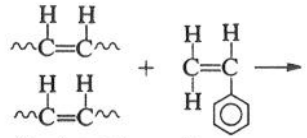
The double bond in the maleic acid is inert toward polycondensation. Note that the degree of unsaturation (average number of double bonds per repeating unit) could be varied from zero to one by employing mixtures of a saturated diacid, e.g., phthalic anhydride (III) with the maleic to form copolyesters with saturated and unsaturated repeating units:



(III)

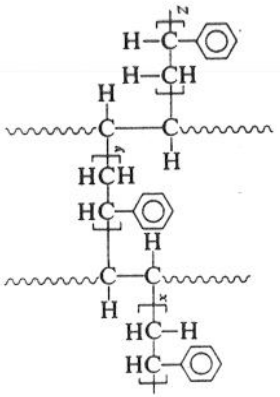
Commercially, the degree of polymerization x is maintained low (say 8–10) (by techniques considered in Chapter 9) so that the product is a viscous liquid.

The linear, unsaturated polyester is then diluted with a liquid vinyl monomer, most often styrene. Before use, a chemical that promotes addition polymerization (Chapter 10) is added, causing the vinyl monomer to undergo addition copolymerization with the double bonds in the polyester to form a highly crosslinked, rigid network:



Unsaturated linear chains

Styrene



Network structure

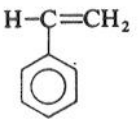
The liquid polyester–styrene mixture is often used to impregnate fiberglass and is cured to form boat hulls, auto (Corvette) bodies, and other so-called fiberglass objects (really fiberglass-reinforced polyester).

Example 4. Show the structural formulas of the repeating units for each of the following polymers and classify them according to structure and chemistry of formation. All the polymers are commercially important. Most follow the rules outlined above, but some don't, and have been included here to illustrate their structures, chemistries of formation, and characteristic linkages.

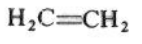
A. Polystyrene
B. Polyethylene
C. Poly(butylene terephthalate) (PBT)
D. Poly(ethylene terephthalate) (PET) (Dacron,® Mylar®)
E. Nylon 6/6 (The numbers designate carbon atoms in the diamine/diacid.)
F. Nylon 6 (The number designates carbon atoms in the monomer.)
G. Glyptal (glycerol + phthalic anhydride)
H. Poly(diallyl phthalate)
I. Melamine-formaldehyde (Melmac,® Formica®)
J. Polytetrafluoroethylene (Teflon TFE®)
K. Poly(phenylene oxide) (PPO) (*Hint*: polymerized in presence of O_2)
L. Polypropylene
M. Acetal (polyformaldehyde or polyoxymethylene) (Celcon®, Delrin®)
N. Polycarbonate (Calibre®, Lexan®, Makrolon®)
O. Epoxy or phenoxy
P. Poly(dimethyl siloxane) (silicone rubber) (*Hint*: polymerized in presence of H_2O)

Q. Polyurethane
R. Polyimide
S. Polysulfone (Udel®)

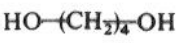
Starting monomers are shown below.

A 

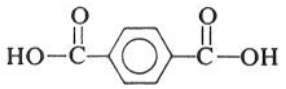
Styrene

B 

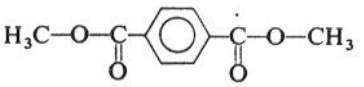
Ethylene

C 

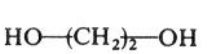
Butylene glycol
(1,4 butane diol)



Terephthalic acid

D 

Dimethyl terephthalate

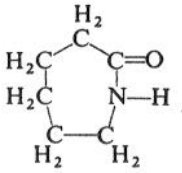


Ethylene glycol

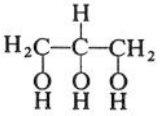
E

Hexamethylene diamine

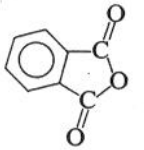
Adipic acid

F 

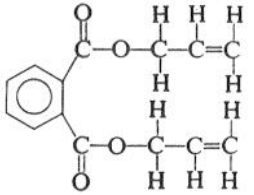
ε-Caprolactam

G 

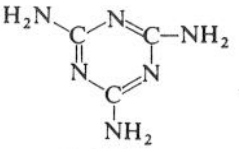
Glycerol



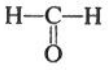
Phthalic anhydride

H 

Diallyl phthalate

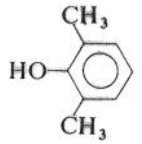
I 

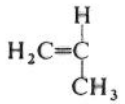
Melamine

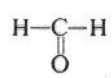


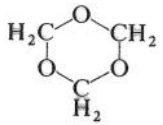
Formaldehyde

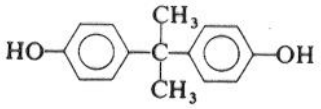
J $F_2C{=}CF_2$
Tetrafluoroethylene

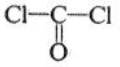
K 
2,6-Dimethyl phenol

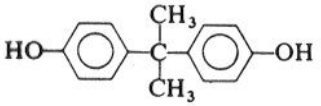
L 
Propylene

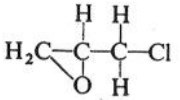
M 
Formaldehyde

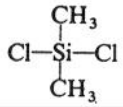
or 
Trioxane

N 
Bisphenol-A

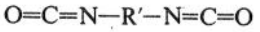

Phosgene

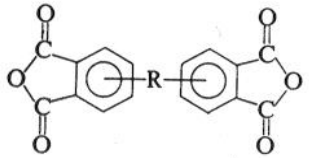
O 
Bisphenol-A


Epichlorohydrin

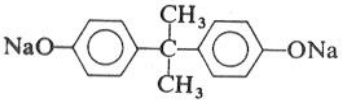
P 
Dimethyl dichlorosilane

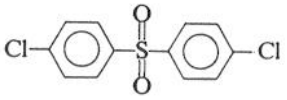
Q HOROH
Diol or glycol


Diisocyanate

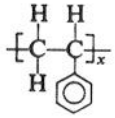
R 
Dianhydride

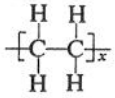
$H_2NR'NH_2$
Diamine

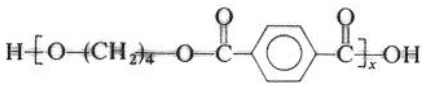
S 

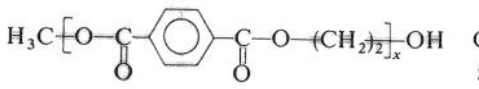


Solution

A 
Linear addition

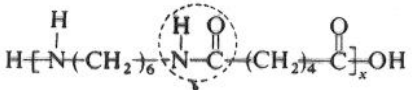
B 
Linear or branched from side reactions, addition

C 
(H_2O out) Linear, condensation

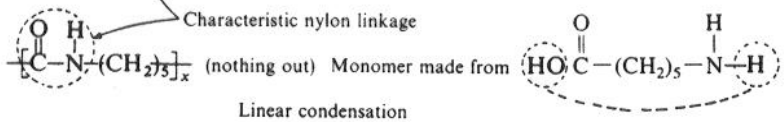
D 
Linear, condensation

CH_3OH
Split out

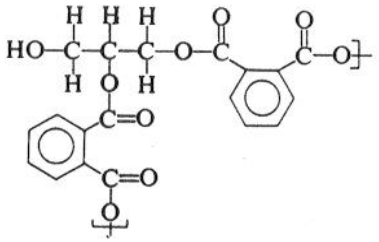
Can also be made from the diacid (see above) splitting out H_2O.

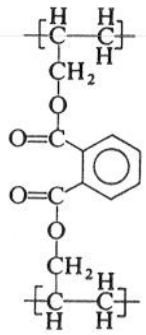
E 
(H_2O out) linear, condensation

Characteristic nylon linkage

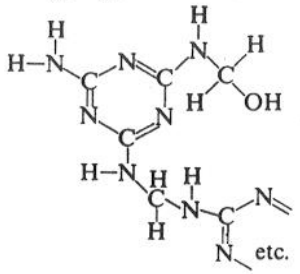
F 
(nothing out) Monomer made from

Linear condensation

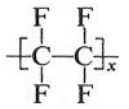
G 
Condensation, structure depends on ratio of reactants (Chapter IX), but usually will be highly crosslinked.

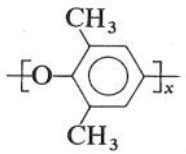
H 
Network, addition

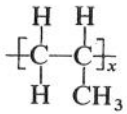
Monomer is 4-functional with two double bonds.

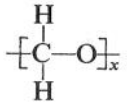
I 
Network, condensation

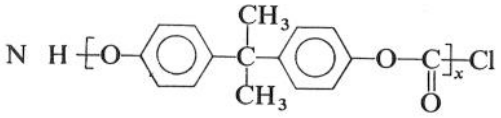
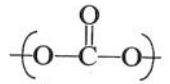
Similar structures result when formaldehyde is condensed with urea or phenol.

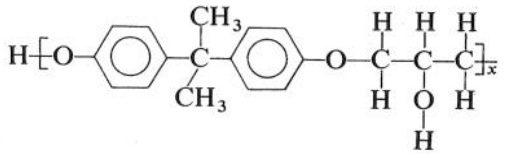
J  Linear, addition

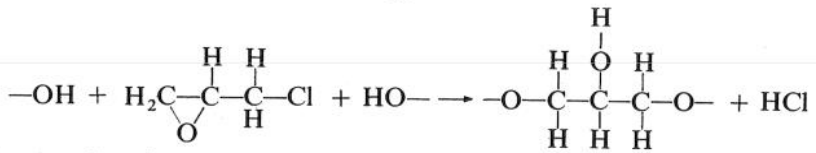
K  Linear, condensation "Oxidative coupling" H_2O out

L  Linear, addition

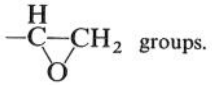
M  Linear, addition Only other double bond that forms addition polymers.

N  (HCl out) Linear, condensation  Characteristic carbonate linkage

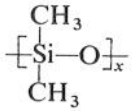
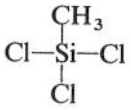
O  *Note*: Get both condensation $-OH + Cl \rightarrow HCl$ and epoxide ring scission.



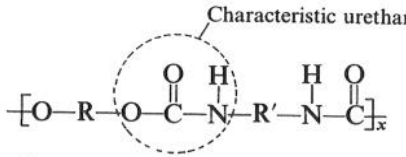
Linear, condensation

for $x < 8$, liquid epoxy
$8 < x < 20$, solid epoxy
} Generally crosslinked later with diamines or acid anhydrides through – OH and terminal  groups.

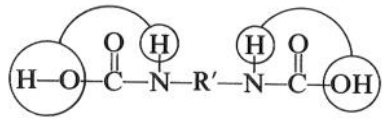
$x \approx 100$, linear, "phenoxy" plastic

P  (HCl out) Linear, condensation Commercial materials contain some  which is 3-functional and allows crosslinking. Also acetate may be substituted for Cl.

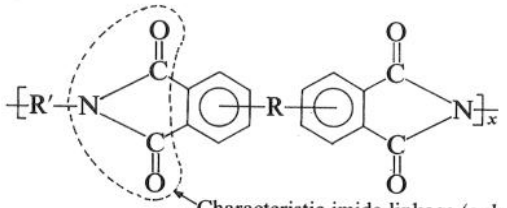
Characteristic urethane linkage

Q  R and R′ vary widely—often R is already a low-x polymer.

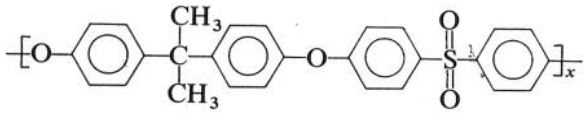
Linear, condensation nothing out, but diisocyanate can be considered.

 minus $2H_2O$

can be crosslinked through amine groups, or by using higher functional alcohols or isocyanates.

R  Linear, condensation

Characteristic imide linkage (only example where both amine H's react).

S  (NaCl out)

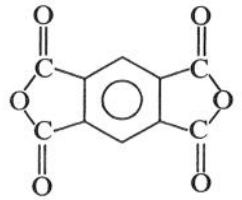
REFERENCE

1. Hounshell, D. A., and J. K. Smith, Jr., *Invention & Technology*, Fall 1988, p. 40.

PROBLEMS

1. A 40-ft "fiberglass" boat hull weighs 3000 lb. Sixty percent of that is a fi cured polyester resin (the remainder is the glass reinforcing fibers, pigme fillers, etc.). What is the molecular weight of the polymer?

2. Pyromellitic dianhydride, PMDA (below), is useful in a variety of polyme ation reactions:



   a. What is its functionality in polyesterification reactions? Structurally, wh type of polymer would you expect to get by reacting PMDA with a glyc

   b. Show the repeating unit of the polymer formed by reacting PMDA w hexamethylene diamine (Example 4E)