

# Polymer Chemistry

The chemical structure and the nature of plastics materials have a significant relationship not only to the properties of the plastic but to the ways in which it can be processed, designed, or otherwise translated into an end-product. Throughout this book the reader will find various references to polymer chemistry (e.g., the section entitled “Theory of Injection Molding,” in Chapter 5 on “Injection Molding”).

This chapter therefore will provide a basic review of polymer chemistry, with emphasis on the distinctions between various structures and their influence on the engineering of plastics products.

## Forming Polymers

Basically, all polymers are formed by the creation of chemical linkages between relatively small molecules or monomers to form very large molecules or polymers; the same idea as connecting boxcars on a railroad to form a train, the boxcars being monomers and the train a polymer. Like boxcars, the molecules must have the ability to be coupled at either end.

Actually, in polymer formation, the process is more like forming many, many trains in a railroad yard simultaneously from the boxcars available in the yard in a competitive fashion, so that the switching engine that moved the fastest would form the longest train while the slowest switching engine would form the shortest train, due to depletion of the available rolling stock by the concurrent train-forming process. The train-forming process of polymerization comes to a stop when factors

prevent any additional boxcars from being added to any of the trains being assembled. Thus, we ultimately end up with trains having a variety of lengths, yet all composed of the same kinds of boxcars.

The railroad analogy described above is basically what happens in an “addition” type of polymerization.

The above process is characterized by the simple combination of molecules without the generation of any by-products formed as a result of the combination. The molecules that combine do not decompose to produce fission products which then remain as part of the reaction debris or need to be removed from the reaction to either allow it to continue the molecule-building process or to ensure the formation of a pure polymer.

In reality the addition-type process can occur in several ways. One way simply involves the external chemical activation of molecules that causes them to start combining with each other in a chain-reaction-type fashion (by the bonding of atoms directly within the reacting molecule). Another way for an addition polymerization to occur is through a rearrangement of atoms within both reacting molecules, but still without the net loss of any atoms from the polymer molecule. And still a third way for addition polymerization to occur is for a molecule composed of a ring of atoms to open up and connect with other ring-type molecules being opened up under the influence of the proper catalytic activators, once again with no net loss of any atoms from the polymer structure.

In another type of polymerization reaction, which has been called “condensation” poly-

merization, the chemical union of two molecules can be achieved only by the splitting out of a molecule (usually small) formed by the atoms, which must be removed from the two molecules being joined to allow the coupling process or polymerization to continue. This is the type of polymerization involved in the formation of some nylons, phenolics, amino resins, and polyester pre-polymers.

Normally the reaction by-product in a condensation type of polymerization must be immediately removed from the reacting polymer because it may either inhibit further polymerization or appear as an undesirable impurity in the finished polymer.

There is yet another method by which polymers may be formed, but it is in reality simply a sequential combination of the previous two processes. Such a process is used in the formation of plastics such as the polyesters and the polyurethanes.

In such a polymerization, a condensation reaction usually is carried out first to form a relatively small polymer, which is then capable of undergoing further reaction by addition polymerization to form larger polymer molecules with a third ingredient. This is what is done when a polyester is formed first by a condensation reaction, and the then still-active polyester is reacted with styrene to form what is essentially a polyester-styrene copolymer.

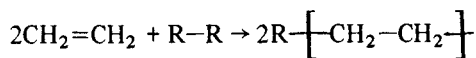
The various types of polymerization reactions are shown in Figs. 2-1a, 2-1b, and 2-1c.

### Polymerization Techniques

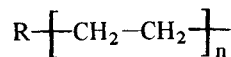
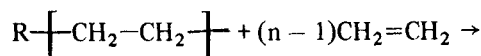
In actual practice there are many different techniques used to carry out polymerization reactions. However, most involve one of four general methods of polymerization: the polymerization of the monomer or reactants in bulk, in solution, in suspension, and in emulsion forms. The bulk and solution methods are used for the formation of both addition and condensation type polymers, whereas suspension and emulsion techniques are used largely for addition polymerizations.

**Bulk Polymerization.** This type of polymerization involves the reaction of monomers or reactants among themselves without placing

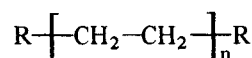
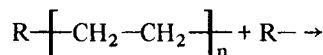
Catalyst activated bond opening (ethylene polymerization)



Initial reaction

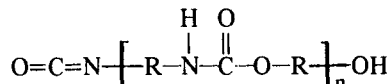
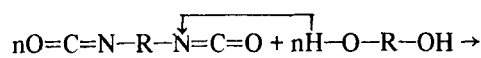


Propagation reaction



Termination reaction (combination)

Rearrangement (polyurethane polymerization)



Ring-opening reaction (nylon 6 from caprolactam)

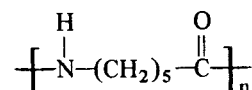
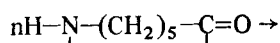


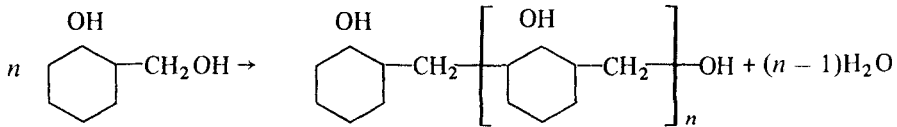
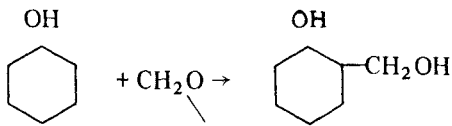
Fig. 2-1a. Typical addition polymerizations (no by-products).

them in some form of extraneous media such as is done in the other types of polymerizations.

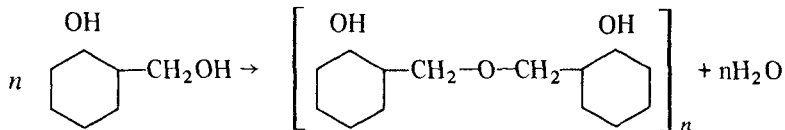
Two types of behavior are observed in bulk polymerizations. In one case, the polymer is soluble in the monomer during all stages of the polymerization, and a monomer-soluble initiator is used. As polymerization progresses, viscosity increases significantly, and chain growth takes place in the monomer or polymers dissolved in the monomer until all of the monomer is consumed.

In the second case, the polymer is insoluble in the monomer system. In such systems, the polymerization is believed to occur within the growing polymer chains because very high molecular weights are formed even though the polymer chain drops out of the monomer solution.

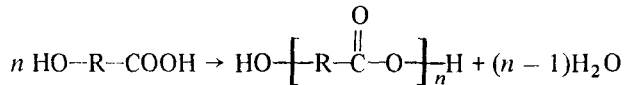
## Phenol-aldehyde reaction



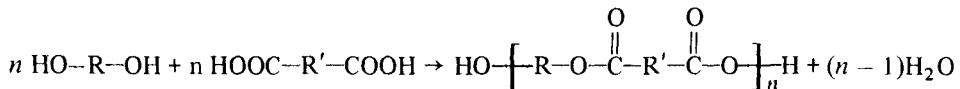
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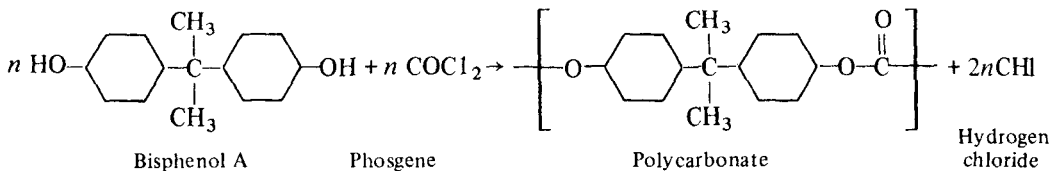
## Polyesterification (reaction between organic acids and alcohols)



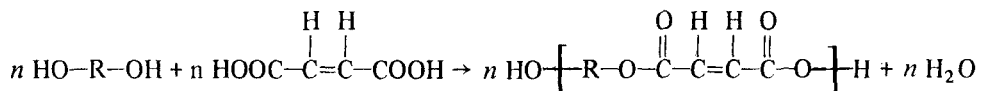
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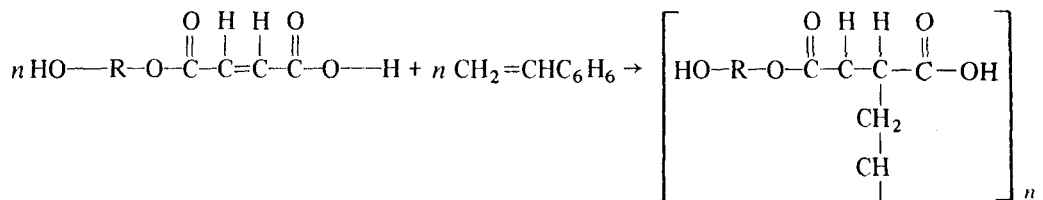
## Reaction when byproduct is other than water (polycarbonate)


**Fig. 2-1b.** Typical condensation polymerizations (production of by-product).

## Step 1: Condensation reaction



## Step 2: Addition reaction


**Fig. 2-1c.** Combination polymerizations (curing of polyesters).

One of the disadvantages of carrying out a polymerization in bulk is the fact that the rise in viscosity can interfere with keeping reaction conditions under control because of the difficulty of maintaining proper agitation and removing heat from exothermic polymerization reactions which give off heat. However, the process is widely used.

*Solution Polymerization.* Solution polymerization is similar to bulk polymerization except that the solvent for the forming polymer in bulk polymerization is the monomer, whereas the solvent in solution polymerization is usually a chemically inert medium. The solvents used may be complete, partial, or nonsolvents for the growing polymer chain.

When the monomer and the polymer are both soluble in the solvent, initiation and propagation of the growing polymer chains take place in the oil or organic phase. Because of the mass-action law, rates of polymerization in solvents are slower than in bulk polymerizations, and the molecular weight of the polymers formed is decreased.

In another case, when the monomer is soluble in the solvent but the polymer is only partially soluble or completely insoluble in the solvent, initiation of the polymerization takes place in the liquid phase. However, as the polymer molecules grow, some of the propagation of polymers takes place within monomer swollen molecules, which are beginning to precipitate from the reaction. When this occurs, it again becomes possible to build up molecular weights because of the decreased dilution within the polymers. Thus, molecular weights as high as those possible with bulk polymerizations can also be achieved in solution polymerizations, provided the polymer precipitates out of solution as it is formed and creates a propagation site.

In the third case, in which the polymer is completely insoluble in the solvent and the monomer is only partially soluble in the solvent, rates of reaction are reduced, and lower molecular weights, below those possible in bulk polymerizations, are formed. However, the formation of relatively high molecular weight polymers is still possible in such a system.

In addition to the relative solubilities of

monomer, polymer, and solvent in the system, the way in which the ingredients are fed to the system can have a significant effect on how the polymerization proceeds, and hence the structure of the finished polymer.

*Suspension Polymerization.* Often called "pearl" polymerization, this technique normally is used only for catalyst-initiated or free-radical addition polymerizations. The monomer is mechanically dispersed in a liquid, usually water, which is a nonsolvent for the monomer as well as for all sizes of polymer molecules that form during the reaction.

The catalyst initiator is dissolved in the monomer, and it is preferable that it does not dissolve in the water so that it remains with the monomer. The monomer and polymer being formed from it remain within the beads of organic material dispersed in the phase. Actually suspension polymerization is essentially a finely divided form of bulk polymerization. The advantage of suspension polymerization over the bulk type is that it allows the operator to effectively cool exothermic polymerization reactions and thus maintain closer control over the chain building process. Other behavior is the same as that of bulk polymerization.

By controlling the degree of agitation, monomer-to-water ratios, and other variables, it is also possible to control the particle size of the finished polymer, thus eliminating the need for re-forming the material into pellets from a melt, as is usually necessary with bulk polymerizations.

*Emulsion Polymerization.* This is a technique in which addition polymerizations are carried out in a water medium containing an emulsifier (a soap) and a water-soluble initiator. It is used because emulsion polymerization is much more rapid than bulk or solution polymerization at the same temperatures and produces polymers with molecular weights much greater than those obtained at the same rate in bulk polymerizations. The polymerization reaction in emulsion polymerization involves causing the reaction to take place within a small hollow sphere composed of a film of soap molecules, called a *micelle*. Monomer diffuses into these micelles, and control of the soap concentration, overall reaction-mass rec-

ipe, and reaction conditions provides additional controls over the reaction.

Polymerization techniques can have a significant effect on the number, size, and characteristics of the polymer molecules formed and thus will have a significant effect on the properties of the polymer. Thus, batches of a polymer such as polystyrene, which can be made by any of the four polymerization techniques described above, will differ, depending on which type of polymerization method was used to make the material.

### Weight, Size, and Distribution of Molecules

Because there is such diversity among polymer molecules, a number of techniques for defining and quantifying these characteristics are in use by the industry—and are also of value to processors and end-users as a determinant of polymer properties.

One such parameter relates to the size of the molecules in the polymer and is known as *molecular weight* (MW). MW refers to the average weight of the molecules in the mixture of different size molecules that make up the polymer. It is expressed either as a number average, based on the sum of the number fractions of the weight of each species or size of molecule present, or as a weight average, based on the weight fractions of each species or size of molecule present in the polymer.

The molecular weight of a polymer has a significant effect on its properties. Thus, higher molecular weight polymers tend to be tougher and more chemically resistant, whereas low molecular weight polymers tend to be weaker and more brittle. In the polyethylene family, for example, low molecular weight polyethylenes are almost waxlike in characteristics, whereas ultra-high molecular weight polyethylenes offer outstanding chemical resistance and toughness (although, conversely, the higher the molecular weight is, the more energy in the form of temperature and pressure required to process the material.)

Another expression applicable to molecular weight is the *degree of polymerization* (DP). This refers to the number of monomer molecules that combine to form a single polymer

molecule and is estimated by dividing the number-average molecular weight of the polymer by the molecular weight of the monomer. The relationship can be expressed as:

$$\text{MW of polymer} = \text{DP} \times \text{MW of monomer}$$

And, finally, it is important to know something about the molecular weight distribution within the polymer, that is, the relative proportions of molecules of different weight. Obviously, if one could create a mono-disperse polymer, all of the molecules would be of a single size. This has not been achieved commercially, however, and so another parameter of definition used to describe polymers is the distribution of the various sizes of molecules within a poly-disperse polymer, that is, the breadth of distribution or ratio of large, medium, and small molecular chains in the resin. If the resin is made up of chains close to the average length, it is called narrow; if it is made up of chains of a wider variety of lengths, it is called broad.

In general, narrow-range resins have better mechanical properties than broad-range resins, although, as with the case of the higher molecular weight materials, they are somewhat more difficult to process.

The molecular weights of polymers and the molecular weight distribution are determined indirectly by measuring the properties of the polymers themselves or of their solutions and correlating this information with the type of molecular weight believed to correspond to the type of property measured.

For example, chemical analysis of the end-groups present in polymer molecules, studies of the boiling points and freezing points of solutions of polymers, and osmotic pressure studies on polymer solutions yield data on the number-average molecular weight of the polymer. Light scattering in polymer solutions and sedimentation methods in the ultra-centrifuge yield data related to the weight-average molecular weights of polymers. Such methods yield the overall average molecular weight of the polymer samples. To get direct data on molecular weight distributions, the polymers first must be

separated by fractionation methods into rather sharp fractions of samples of relatively monodisperse molecular weight.

## Polymer Structure

In addition to the size of molecules and the distribution of sizes in a polymer, the shapes or structures of individual polymer molecules also play a major role in determining the properties of a plastic.

Earlier, in the discussion of the analogy between the connecting of railroad boxcars to form a train and the formation of polymers, it was implied that polymers form by aligning themselves into long chains of molecules without any side protrusions or branches, or lateral connections, between molecules. Some polymers do largely this and nothing more; however, it is also possible for polymers to form more complex structures. Thus, polymer molecules may form in the shape of branched molecules, in the form of giant three-dimensional networks, in the form of linear molecules with regular lateral connections to form "ladder-type" polymers, in the form of two-dimensional networks or platelets, and so forth, depending on how many connections or bonds can exist between the monodisperse monomeric molecules that were used to form the polymer and between sites on the forming or already formed polymer molecules. See Fig. 2-2.

Because of the geometry of such molecules, some can come closer together than others in which the structure prevents more intimate contact. The structural obstruction to close approach is called *steric hindrance*. Thus, polymers that can be packed closely or exhibit little steric hindrance ordinarily can more easily form crystalline structures in which the molecules are aligned in some regular pattern; others, such as polymers that are cross-linked prior to crystallization, are prohibited from aligning themselves in crystals because of the hindrance created by the multiple interconnections and hence tend to be amorphous, or noncrystalline.

Amorphous polymers do not have melting points, but rather softening ranges; are normally transparent; and undergo only small vol-

ume changes when solidifying from the melt, or when the solid softens and becomes fluid. Crystalline polymers, on the other hand, have considerable order to the molecules in the solid state, indicating that many of the other atoms are regularly spaced; have a true melting point with a latent heat of fusion associated with the melting and freezing process; and have a relatively large volume change during the transition from melt to solid.

Thus, many different structures are possible with plastics—and each will affect the basic properties of the polymer. For example, linear polymers, such as high-density polyethylene, are made of molecules that resemble spaghetti in a bowl and are relatively free to slide over one another or to pack more closely together (in the absence of steric hindrances due to large pendant side groups). Branched polymers, such as low-density polyethylene, on the other hand, have side appendages and interconnections that cause the molecules to resemble clumps of tree branches that cannot be easily compressed or compacted. Thus, branched polymers (with more voids) are more permeable to gases and solvents than linear polymers, lower in density (since the molecules are not compacted together), and more flexible. Linear polymers, on the other hand, are higher in tensile, stiffness, and softening temperatures.

Cross-linked structures, in which the individual chain segments are strongly bound together by chemical unions, also have special characteristics (as in the family of thermosetting plastics). They do not exhibit creep or relaxation unless such primary bonds actually are broken by continually applied stress or by elevated temperatures high enough to cause chemical decomposition of the polymer. Cross-linked polymers also are fairly resistant to solvent attack; solvents may swell such polymers, but seldom cause complete rupture or dissolution.

Ladder structures have unusual stability and have become important in terms of the new heat-resistant plastics. Aromatic compounds (such as benzene) and heterocyclic compounds (such as benzimidazole) that have semiladder, ladder, or spiro structures offer heat stabilities in excess of 900°F.

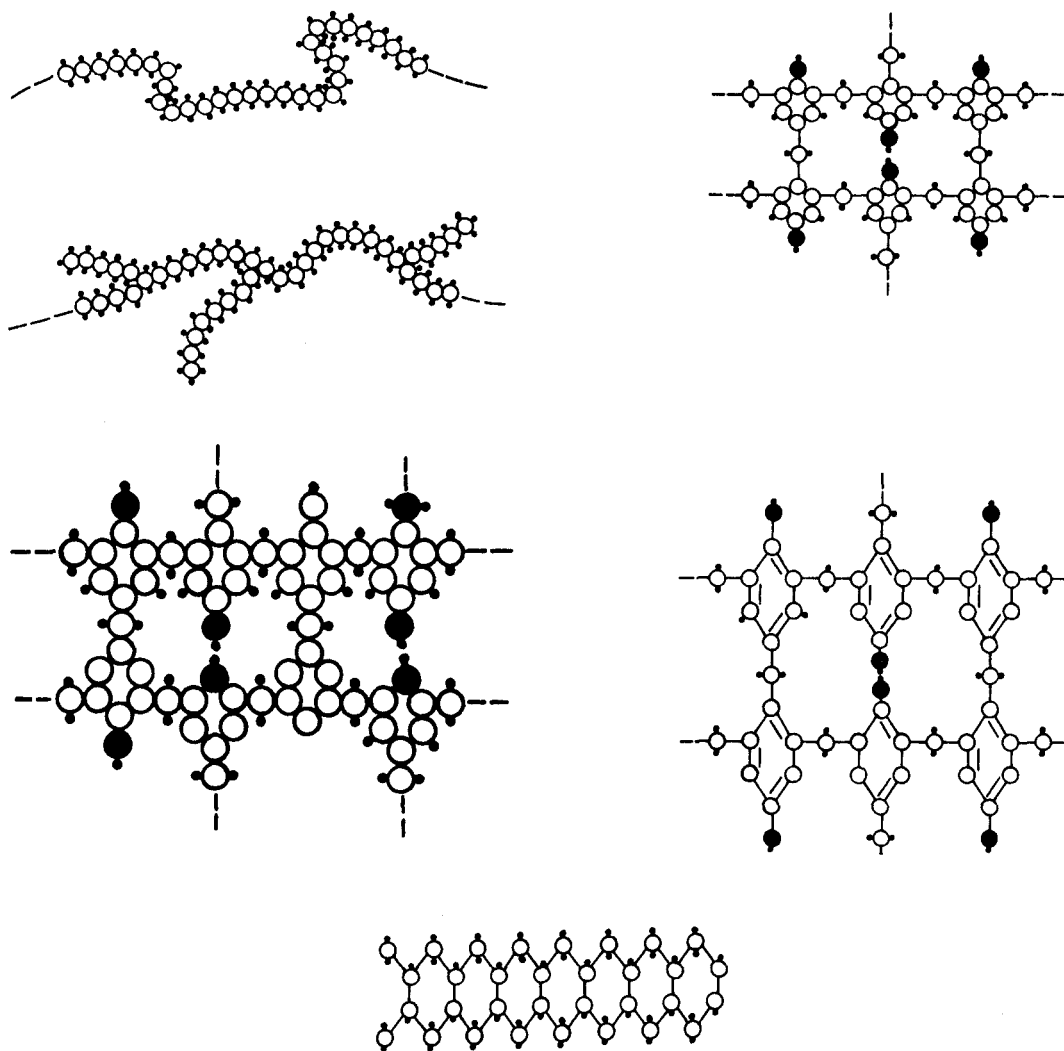


Fig. 2-2. Types of molecular structures in polymers.

### Effect of Time and Temperature

It should also be noted that whereas the effect of molecular weight and molecular weight distribution on properties is relatively fixed and stable with temperature (barring decomposition of the polymer), the arrangement of the molecules within the structure of a polymer mass is in most cases relatively sensitive to temperature. Thus, the structure of any given polymer can be significantly changed by exposing it to different temperatures and thermal treatments.

For example, heating a crystalline-type polymer above its melting point and then quenching

it can produce a polymer that is far more amorphous or noncrystalline in structure than the original polymeric sample. Such a quenched material can have properties that are significantly different from the properties of a sample that is cooled slowly and allowed to recrystallize.

The effects of time on a polymer structure are similar to those of temperature in the sense that any given polymer has a "most preferred" or equilibrium structure in which it would prefer to arrange itself, but it is prevented from doing so instantaneously on short notice by steric hindrances. However, given enough

time, the molecules in a polymer ultimately migrate to arrange themselves in this form. Elevating the temperature and making the molecules more mobile or spreading them apart allows them to accomplish this in a shorter time and vice versa.

Thus over an extended period of time, the properties of a polymer can become significantly different from those measured earlier if the structure of the polymer was in an unstable form when the properties were initially evaluated.

### Chemical Composition

In addition to all the variations in the makeup of the polymer discussed above and having to do largely with extra- or intermolecular phenomena, polymer properties also are heavily dependent on such factors as the intramolecular chemical composition of the polymer

For example, as shown in Fig. 2-3, polyethylene consists (except for catalyst or extraneous impurities) completely of atoms of carbon and hydrogen. This internal makeup of the

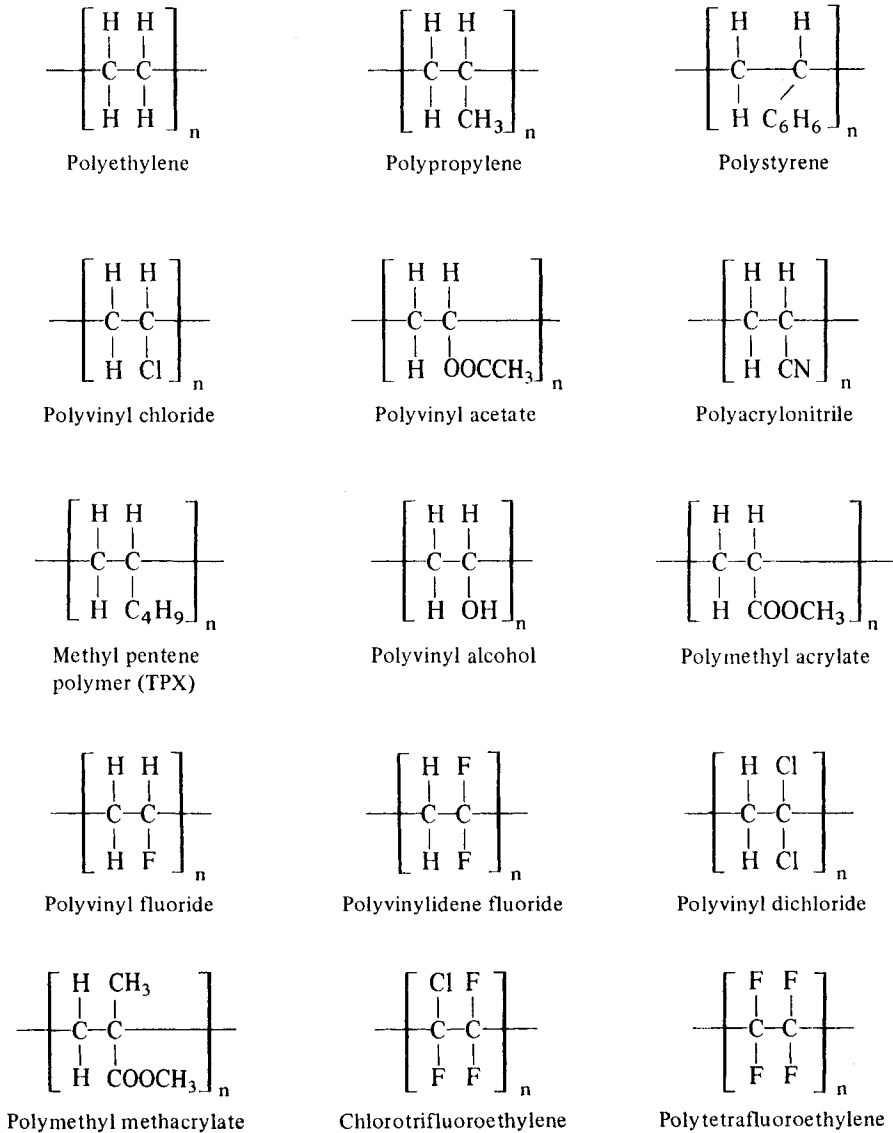


Fig. 2-3. Polymers based on the ethylene chain.

polymer molecule affects in turn all the previously discussed variables and hence contributes its own basic characteristics to the overall properties of the polymer.

Going further, if one takes every fourth hydrogen atom occurring in polyethylene and replaces it with a methyl ( $\text{CH}_3$ ) group in regular intervals along the length of the chainlike molecule as shown in Fig. 2-3, the polyethylene is transformed into polypropylene. In such a case,<sup>2</sup> the degree of polymerization and the molecular weight distribution remain roughly the same; but the spacing of the molecules in the polymer matrix or the morphology of the polymer changes, and thus its macroscopic physical properties also change.

Similarly, if every fourth hydrogen atom of the polyethylene were substituted with a benzene ring structure ( $\text{C}_6\text{H}_6$ ), or with a chlorine atom (Cl), as shown in Fig. 2-3, the ethylene would become either polystyrene or polyvinyl chloride, respectively.

The simple substitution of a single hydrogen atom with another atom or chemical group can cause a drastic change in the properties of a polymer. Whereas polyethylene is translucent, flexible, and crystalline, polystyrene is transparent, brittle, and amorphous.

## Copolymers

In addition to making changes in the basic repeating unit by substitution, as illustrated above, it is possible to change the chemical composition and hence the morphology and properties of a polymer by mixing the types of structural groups or basic repeating units within the chain of a polymer. This is done by a process called *copolymerization*. In such a reaction, for example, monomers of styrene and acrylonitrile can react to form styrene-acrylonitrile copolymers; or styrene may react with butadiene to form styrene-butadiene copolymers; or acrylonitrile, butadiene, and styrene may all react simultaneously to form the ABS (acrylonitrile-butadiene-styrene) copolymers. Any of the polymerization techniques previously discussed can be used.

In addition to varying the types of starting ingredients used to form copolymers, the rela-

tive amounts of each monomer used in the reaction also may be varied to produce a literally unlimited number of possible permutations and combinations of types and amounts of monomers. The ability of the polymer chemist to react different monomers together in different amounts has given rise to the concept of "tailor-making" plastic materials.

Figure 2-4 illustrates some of the more common copolymers now available commercially. The subscripts of  $x$ ,  $y$ , and  $z$  denote differing amounts of each of the structural units in the polymer chain. It should be noted that the structural formulas in Fig. 2-4 are somewhat fictional, in the sense that there is an implication that a long chain of one group is connected to a long chain of another group, and successively to a long chain of still a third type of polymer. Actually, the distribution of each of the species within the chain will depend both on the amount present and how the polymerization was carried out.

For example, an acrylonitrile-styrene copolymer might be made by first reacting a good portion of the acrylonitrile to form polyacrylonitrile and then adding the styrene and remaining acrylonitrile to complete the polymerization of the desired end product. Or, in another case, both ingredients might be added to a reactor simultaneously and allowed to react concurrently.

## Other Polymers

From a study of Figs. 2-3 and 2-4, it will be noted that all of the polymers listed there are formed by combinations made possibly by reaction of the double bonds that exist between adjacent carbon atoms in the monomers used as starting materials. However, as mentioned earlier, this is not the only way in which polymers are formed. When polymers are created by rearrangements or condensation reactions, other types of polymeric chains can be formed. Figure 2-5 lists the structural formulas of several commercially important polymers in which oxygen (O) is an integral part of the bonds holding the polymer together. Similarly, Fig. 2-6 lists several types of polyamides and a polyurethane in which nitrogen (N) atoms form

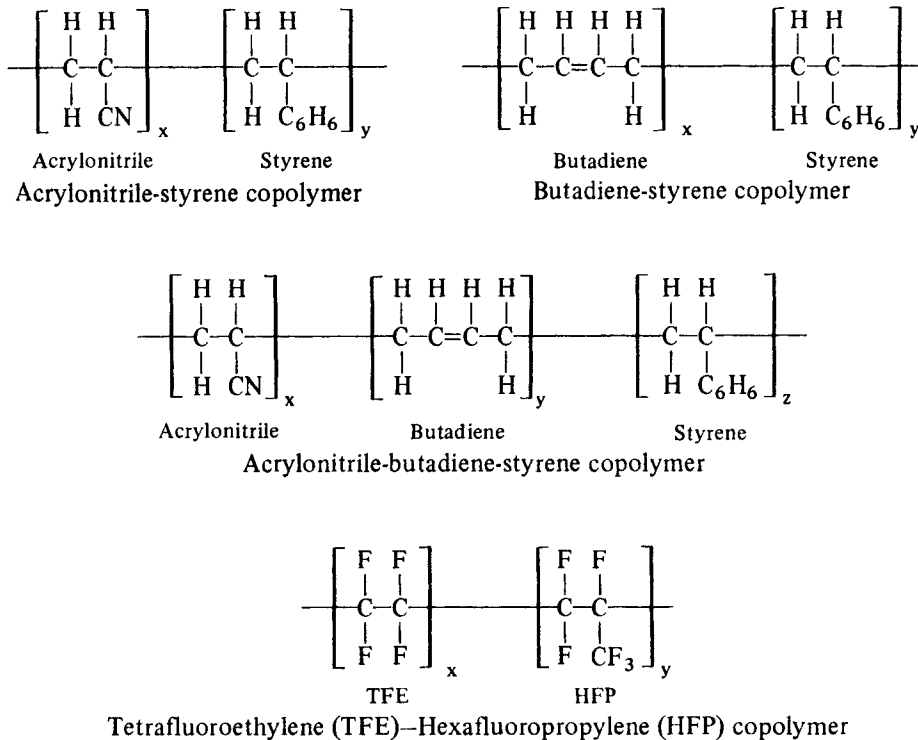


Fig. 2-4. Carbon "backbone" copolymers.

the bonds between portions of the polymer molecule. In some cases the polymers are formed by molecular rearrangements (in the case of polyurethanes and epoxies) and in other cases by condensation reactions (some nylons).

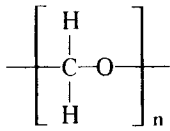
Other condensation polymers are illustrated in Fig. 2-7, which shows some of the complex structures proposed for the more common types of thermosets. Note that the thermosets always have more than two linkages connecting the various structural units in the polymer, and they are commonly referred to as cross-linked materials involving a networklike molecular structure.

There are at least 30 to 40 different families of thermoplastics now offered and about 10 different basic families of thermosets. And this takes into account only the more common types of polymers. It should also be noted that copolymers, mixtures, and chemically modified versions of the polymers listed make the total number of polymeric materials that are theoretically possible entirely too great to list them in any one place.

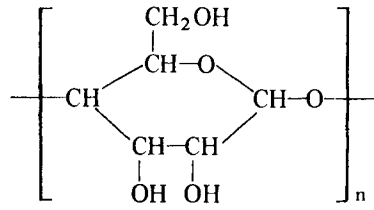
In addition, the properties of a polymer may be radically altered by mixing it with non-polymeric materials and chemicals. In fact, some polymers would be worthless to the molder or extruder if additives were not used to modify them before they were processed into finished products.

For example, phenolic, urea, and melamine resins, as they come out of the polymerization kettle, are largely brittle, frangible solids with low impact strength. To make them usable, such materials must be mixed with a filler of some kind to reinforce the strength of the polymer. In the case of the three thermosets mentioned, cellulose fillers made from wood flour or cotton are necessary to make the resins commercially moldable. Similarly, cellulose and vinyl resins must also be mixed with semisolvents, called *plasticizers*, to soften them to some degree (so they may be molded or extruded) or to modify their properties (to make them soft and pliable, rather than hard and stiff).

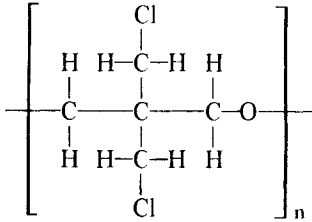
In actual practice, the number of different



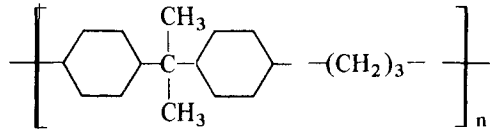
Polyacetal resin



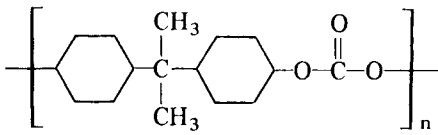
Cellulose (natural polymer)



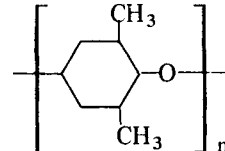
Chlorinated polyether



Phenoxy resin (polyhydroxyether)

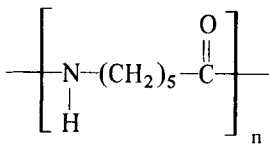


Polycarbonate

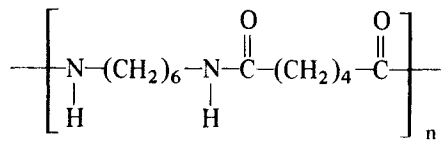


Polyphenylene oxide

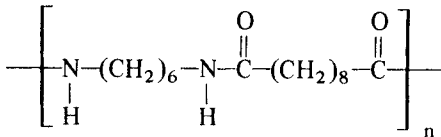
Fig. 2-5. Polymers with oxygen in the chain.



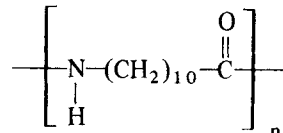
Nylon 6



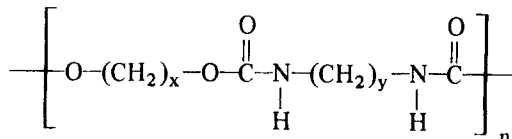
Nylon 6/6



Nylon 6/10

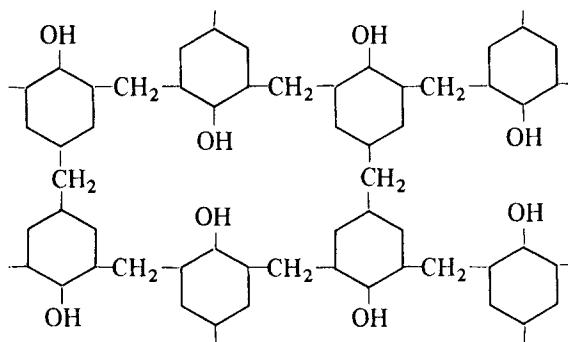


Nylon 11

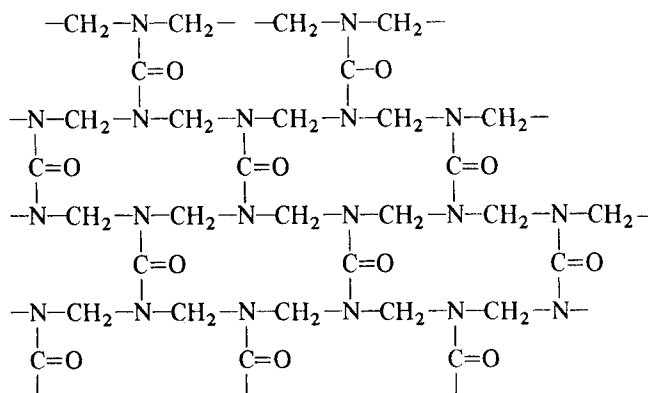


Polyurethanes

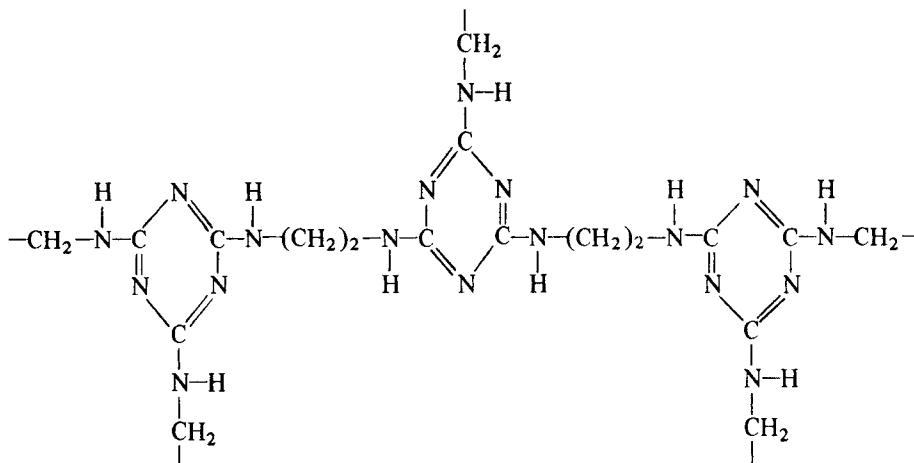
Fig. 2-6. Polymers with nitrogen in the chain.



Phenol-formaldehyde resin



Urea-formaldehyde



Melamine-formaldehyde

Fig. 2-7. Thermoset structures.

types of chemical additives and fillers that are mixed with the fundamental polymer is so large that the chemistry of plastic compounds becomes extremely complex.

It also is possible to vary existing polymers by any number of chemical, mechanical, or irradiation techniques to change the structure of the polymer. During processing, for example, it is possible to align or orient the molecules in

a polymer to significantly increase the strength of the polymer in the direction of the orientation. Chemical or irradiation methods also can be used to cross-link a plastic (such as polyethylene) to improve its toughness and chemical resistance. Nucleation techniques and chemical modification (as in the case of chlorinated polyethylene) are further adaptable to changing polymer structures.