

# Aging of Polymers

by David L. Allara\*

This paper provides background on the basic chemical processes which can occur during the exposure of polymers to typical end-use environments such as air, sunlight, water vapor, and various atmospheric pollutant gases.

## Introduction

The use of polymers as materials for manufacture of many everyday items is constantly increasing. The large number of polymers available allow wide variation in physical properties such as toughness, appearance, and processing ease. However, all polymers are ultimately susceptible to chemical degradation under exposure to various conditions of commonly encountered environments. If one excludes more aggressive conditions such as high energy radiation, large concentrations of corrosive gases, and high temperature such as encountered in combustion, a large number of polymers are still quite susceptible to slow chemical degradation. The chemical changes which occur during such degradation, as a general consideration, deserve evaluation as regards alterations in any implications for health aspects of the polymers' end uses. An understanding of the basic chemical mechanisms involved in the degradation process is therefore significant. In this paper the environments considered are those which can be arbitrarily classed as "habitable." These are defined as those with temperatures below 100°C, an atmosphere of air (with and without typical pollutants), varying amounts of water, present as vapor or liquid, and light (sunlight and artificial). Normally, polymers in the state of their end-use are not pure materials. In many cases there are added substances which alter the engineering and/or chemical properties of

the polymer in a useful way. The polymer also may contain small amounts of monomer, entrapped during the polymerization process. Such additives and impurities may participate in the slow chemical degradation of the polymer and, of course, add to the general physical complexity of the polymer. However, for purposes of establishing basic chemical mechanisms this paper will discuss only the degradation of pure polymers.

Since a polymer is a repeating chain of simple chemical functional groups linked together, the usual types of chemical reactions that the individual functional units undergo in small molecules also apply to a polymer of these groups. However, the rates at which these reactions take place are often altered because of morphological effects in the solid polymer which are not present in solutions and vapors of simple organic molecules. In general, because of the difficulty encountered with the penetration of chemical agents and radiation (e.g., sunlight) into a solid polymer, chemical degradation rates are usually considerably slower for the polymer than for small organic molecules made from the same functional groups. Degradation may be initiated several ways. Absorption of ultraviolet radiation and/or thermal energy can lead to rupture of weak bonds. This is often followed by formation of new bonds to give an alteration of the original polymer structure. The presence of oxygen, water and atmospheric pollutants can alter these processes and lead to the formation of new types of chemical groups. Bond-breaking processes may occur in polymer backbone bonds to lower the average length of

\* Bell Laboratories, Murray Hill, New Jersey 07974.

the polymer chains and/or in pendant group bonds leading to the emission of small molecules. Bond-making processes between chains give crosslinked material of increased molecular weight and rigidity. All of these effects will be discussed in the next section. More detailed reviews of these processes can be found elsewhere (1-4) and the reader is encouraged to consult these references for a more comprehensive view of the field.

As a final note of introduction, it is important to realize that although the basic qualitative processes involved in degradation of common polymers are reasonably well determined, the present quantitative understanding, in general, is insufficiently advanced in order that quantitative predictions can be made of the extent of degradation and the levels of products (particularly minor ones) under typical environmental exposures. In addition, for such predictions one needs to know exactly such variables as temperature variations, light flux and wavelengths, processing conditions, localized concentrations of reactive gases, and the nature of any additives. Unfortunately, these usually cannot be easily evaluated and thus quantitative predictions of chemical degradation are rendered difficult. More studies aimed at allowing predictions of levels of degradation products of interest would be most welcome in this field. Accordingly, the discussion presented here is intended to be quite broad in scope and detail is thus necessarily restricted.

## Reactions Requiring No External Molecules

These are reactions which occur thermally and/or photolytically. The basic reactions are shown in Figure 1. When external radiation is absent, these reactions are generally unimportant below 100°C, with a few exceptions (see below). In the presence of light the degradations are sometimes greatly accelerated if an absorbing chromophore group is present, e.g., carbonyl groups, hydroperoxides, imino groups, aromatic rings and conjugated C=C bonds.

Degradation of common polymers by thermally induced rupture of random chain links can be regarded as unimportant at ambient temperatures. However, with strong radiation such processes may occur in certain polymers. Other reaction paths such as depolymerization or elimination may be regarded as more likely routes of thermal degradation.

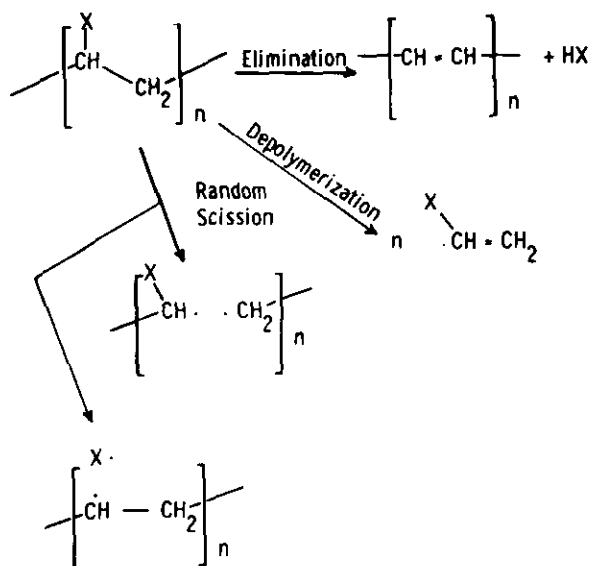
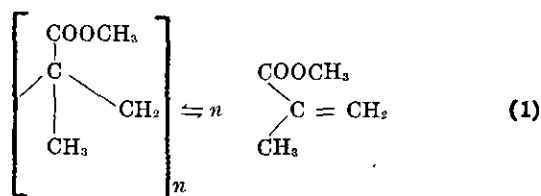


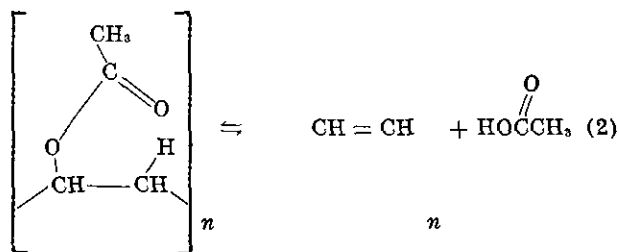
FIGURE 1. Various energy-induced processes of degradation.

A typical example of a depolymerization process is the degradation of poly(methyl methacrylate). This polymer depolymerizes extensively [eq. (1)] upon strong heating. However, at 100°C it can be estimated that it will take about  $10^{15}$  yr for 50% of the material to depolymerize.

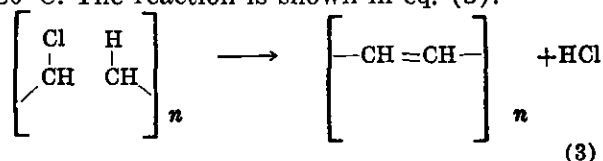


Since poly(methyl methacrylate) depolymerizes at temperatures considerably lower than most other common polymers, one can make the general conclusion that degradation of common polymers by depolymerization is not significant at ambient temperatures.

An excellent example of a very facile elimination is given by the thermal degradation of poly(vinyl acetate) [eq. (2)].



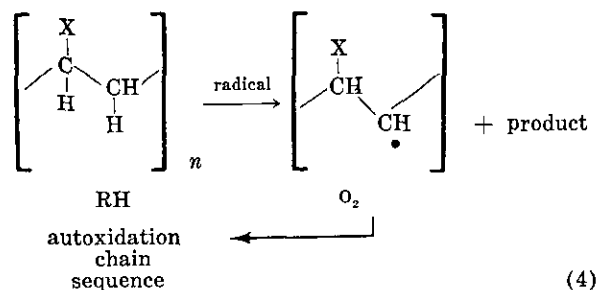
This material degrades very cleanly to acetic acid and a C=C chain bond, and it can be estimated from higher temperature data that it will take about 20 yr for 50% degradation at 100°C. Since most other polymers are much more stable to such elimination reactions, one can conclude that at ambient temperatures purely thermal elimination reactions are unimportant. However, one notable exception of a common polymer which gives measurable elimination at low temperatures is poly(vinyl chloride). Careful studies (5) have shown that measurable HCl evolution can occur in days at 80°C. The reaction is shown in eq. (3).



The mechanism is quite complex and controversial. It may be a blend of ionic and free-radical processes, but the only significant product reported at lower temperatures is HCl. The HCl evolution can be greatly accelerated by light and oxygen, depending upon such factors as the amount of oxygen present and the wavelength and intensity of the light.

## Reactions with O<sub>2</sub>

Thermal and photo-oxidative degradation are the most common types of deterioration mechanisms. A partial scheme of the autoxidation process is shown in eq. (4) for oxidation of C-H groups.



The reaction sequence is initiated by some trace amount of free radicals or atoms which can abstract a hydrogen atom from a C-H group to produce a radical site which can react with O<sub>2</sub>. A complex, free-radical chain reaction ensues as shown in Figure 2. (Other X-H groups, where X is not carbon are possible, but C-H

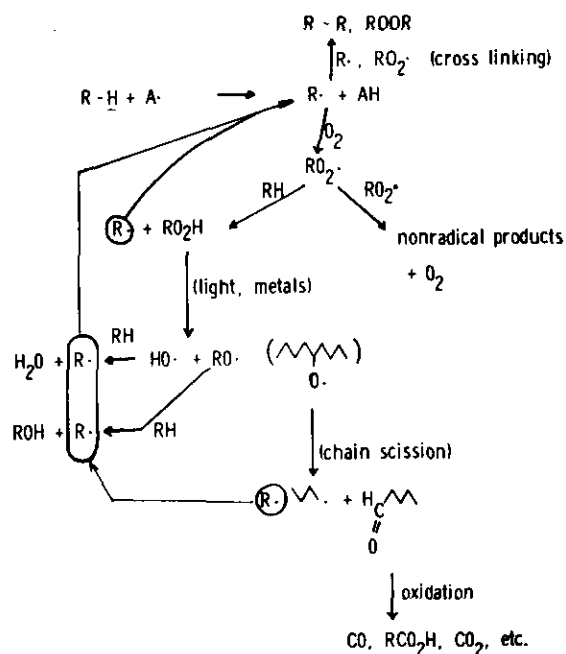


FIGURE 2. Free-radical chain-oxidation sequence for polymers with susceptible C-H bonds.

is overwhelmingly the most common). The C=C group is also quite susceptible to attack by free radicals and leads to an oxidation sequence which is similar to that for C-H oxidation. The eventual result of autoxidation is formation of oxygenated functional groups in the polymer backbone (carbonyl groups, alcohols, ethers and hydroperoxides), chain scission leading to lower chain sizes, occasional cross-links (ether or peroxide) between chains, and emission of small molecules such as CO, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, and small organic molecules such as carboxylic acids and ketones. The presence of metal particles or salts often accelerates the oxidation. This is usually regarded as due to catalysis of the homolysis of hydroperoxide molecules into reactive radicals. More detailed discussions of these processes can be found elsewhere (1). A typical time for ~1% reaction of a susceptible polymer (with no additives) such as polyethylene could be several years at ambient summer temperatures. The types of polymers susceptible to thermal-oxidative attack are shown in Figure 3 with the general types of products formed. It should be noted that poly(vinyl chloride) is quite readily degraded in the presence of oxygen; the major product is HCl, and the mechanism is quite complex.

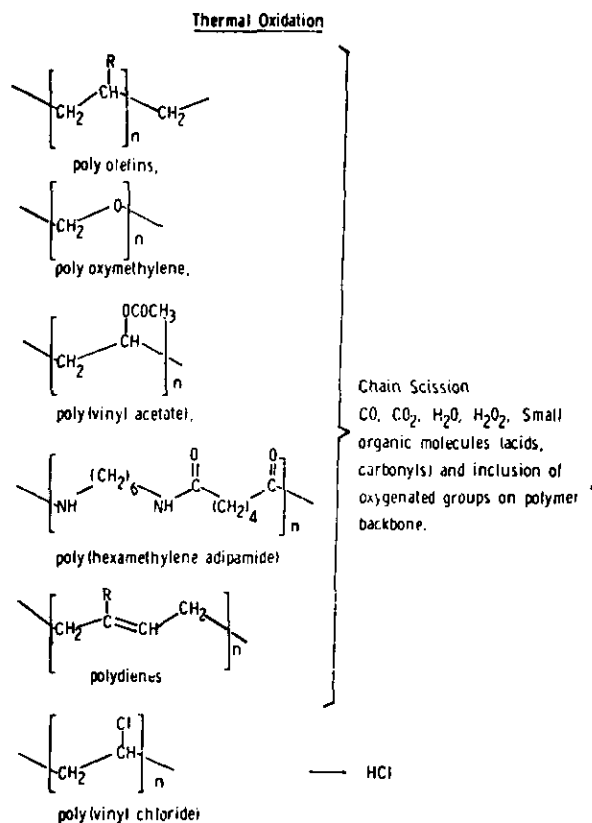


FIGURE 3. Selected polymers susceptible to thermal oxidation and their products.

The processes of oxidative degradation can be greatly accelerated by ultraviolet radiation. The absorption of light energy by sensitive groups (e.g., hydroperoxides or carbonyl groups) can result in the formation of reactive species by bond rupture or in some cases just by the formation of suitable electronically excited states (e.g., singlet oxygen). These species often can accelerate the normal free-radical chain oxidation as well as provide new degradation paths. The net effects of photo-oxidation are roughly the same as thermal oxidation, e.g., formation of backbone carbonyl groups, chain scission, and production of  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and other small molecules. Some general types of polymers which photooxidize are shown in Figure 4. Polymers susceptible to thermal oxidation are also sensitive to photo-oxidation. In addition, polymers with strong ultraviolet absorbing groups are often quite susceptible even though stable to thermal oxidations. Photo-oxidation normally occurs mostly in the surface

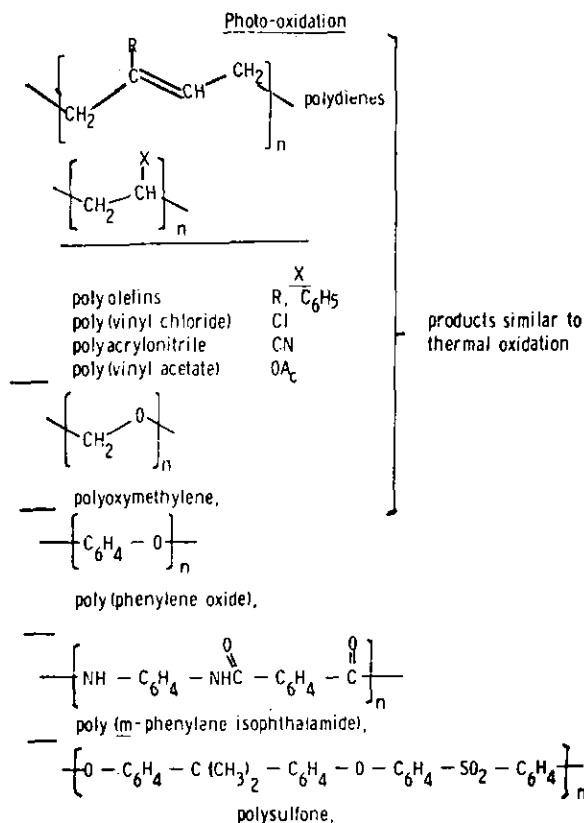


FIGURE 4. Selected polymers susceptible to photo-oxidation.

regions of the polymer because of combinations of such effects as oxygen diffusion and the opacity of the polymer to the radiation. In general, fundamental studies have only been done on a few types of polymers (1).

## Hydrolysis

Functional groups such as esters, amides, and acetals can be attacked by water to form the parent acid or aldehyde group and the corresponding alcohols or amines in the first two cases. When the hydrolysis-sensitive bonds are part of the polymer backbone chain links, hydrolysis will result in depolymerization and release of the hydrolyzed monomers from the polymer. When the functional groups are attached to the side of the backbone chain, the polymer remains intact but small molecules are released. Examples of hydrolyses are given in

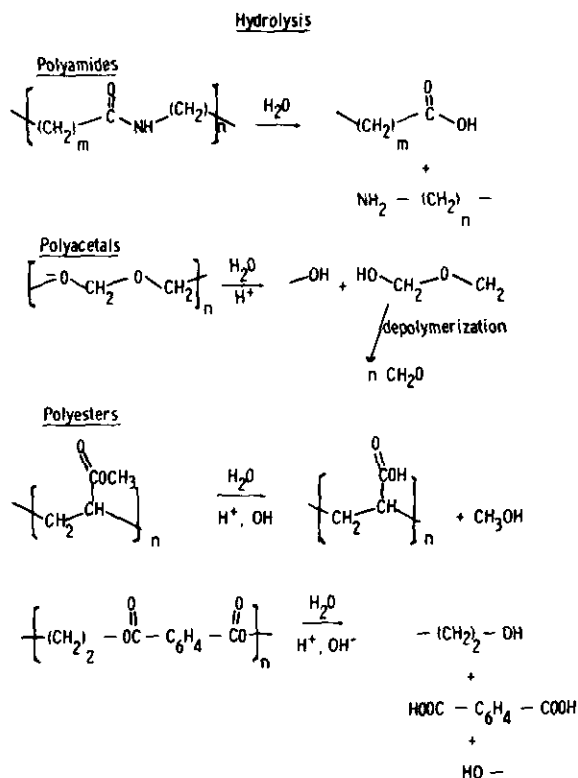


FIGURE 5. Hydrolysis reactions of representative polymers.

Figure 5. Some hydrolyses require acid or base catalysis and often these catalysts can be supplied by external agents, such as atmospheric  $\text{SO}_3$ , or oxidation products of the polymer. Penetration of water into many polymers is surprisingly great, but in many cases hydrolysis (like oxidation) may be restricted to surface regions.

### Other Active Molecules

There are several atmospheric gases which are often present in sufficient amounts to affect

the properties of polymers. The most common of these is ozone which is responsible for the severe cracking of many rubber products, particularly in urban atmospheres. This agent is quite reactive toward  $\text{C}=\text{C}$  bonds and rapidly breaks them with the formation of carbonyl compounds on the new chain ends. Such reactions are normally restricted to the surface of the polymer, since the  $\text{O}_3$  is too reactive to penetrate far into the polymer bulk.

The oxides of sulfur and nitrogen— $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{NO}$ , and  $\text{NO}_2$ —can react with polymers in the absence and presence of light to give a complex variety of results. The oxides of sulfur can cause sulfonation reactions, catalyze photo-oxidation, and in the presence of water produce strong acids which can catalyze hydrolysis. Similarly, nitrogen oxides can cause nitration reactions and act as photo, free-radical, and acid catalysts. Reactions of  $\text{SO}_2$  and  $\text{NO}_2$  with polymers has been reviewed and studied by Jellinek (6). Health hazards associated with the degradation of the polymer to give the formation of harmful products would appear secondary to the presence of these very reactive reagents themselves.

### REFERENCES

1. Hawkins, W. L., Ed. *Polymer Stabilization*, Wiley-Interscience, New York, 1972.
2. Nieman, M. B. *Aging and Stabilization of Polymers*. Consultants Bureau, New York, 1965.
3. Reich, L., and Stivala, S., *Autoxidation of Hydrocarbons and Polyolefins*, Dekker, New York, 1969.
4. Grassie, N. *Degradation*. In: *Encyclopedia of Polymer Science and Technology*, Vol. 4, Interscience, New York, 1966, p. 647.
5. Palma, G., and Carena, M. *Degradation of poly(vinyl chloride)*. I. Kinetics of thermal and radiation-induced dehydrochlorination reductions at low temperatures. *J. Appl. Polym. Sci.* 14: 1737 (1970).
6. Jellinek, H. H. G. *Polymer-gas reactions (air pollutants:  $\text{NO}_2$  and  $\text{SO}_2$ ) as function of pressure, UV light, temperature and morphology—a survey*. In: *Proceedings of the 4th Materials Research Symposium, 1970, Garthersburg, Md., National Bureau of Standards Special Publication 357, Washington, D.C., 1972.*