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Bengt Rånby^a

^a Department of Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden

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BASIC REACTIONS IN THE PHOTODEGRADATION OF SOME IMPORTANT POLYMERS

BENGT RÅNBY

Department of Polymer Technology
The Royal Institute of Technology
S-100 44 Stockholm, Sweden

INTRODUCTION

It has been known for hundreds of years that native organic materials like textile fibers from cotton and flax are degraded in sunlight and lose strength by outdoor exposure. This phenomenon was studied in the 1800s when fibers and textiles were bleached to increase their whiteness. The molecular mechanisms involved were not known at that time. The chain structure of cellulose was established much later through the macromolecular concept, formulated by Herman Staudinger in 1920, and generally accepted by scientists in the 1930s. On a macromolecular basis, important advances in understanding the chemical reactions involved in photodegradation of polymeric materials have been made since about 1940. Plastics, rubber, fibers, paint, and lacquers are all degraded in sunlight by basically the same free radical mechanisms extensively studied for 50 years [1]. Polymers show different inherent photostabilities when they are used as materials. Depending on their resistance to photodegradation, polymers can be divided into groups showing different degrees of stability [2].

POLYMERS OF DIFFERENT PHOTOSTABILITIES

Highly photostable polymers are commonly used without any photostabilizer added, e.g., poly(tetrafluoroethylene) and poly(methyl methacrylate), with an outdoor lifetime of many years.

Moderately photostable polymers can be used outdoors without any photosta-

bilizer added, e.g., poly(ethylene terephthalate), polycarbonates, poly(vinyl fluoride), and poly(vinylidene fluoride), with an outdoor lifetime of a few years.

Poorly photostable polymers need extensive photostabilization for outdoor use, e.g., polyolefins, polystyrene, poly(vinyl chloride), aliphatic and aromatic polyamides, polyurethanes, diene rubbers, polymeric coatings, cellulose, and cellulose derivatives with an outdoor lifetime of less than a year when compounded without any photostabilizer added.

EARLY STUDIES OF PHOTODEGRADATION

Systematic studies of photodegradation and photostabilization of polymers were started in the 1940s when it was observed that photoinitiated degradation in air also involves a simultaneous oxidation. The basic mechanism of photooxidative degradation was established by Bolland and Gee in the 1940s [3]. The mechanism involves an *initiation reaction* of free radical formation by chain scission or some other bond cleavage which in outdoor exposure is caused by the ultraviolet radiation in sunlight. A rapid subsequent reaction is addition of molecular oxygen to the polymer radicals. The peroxy radicals formed abstract hydrogen from adjacent chains and give unstable hydroperoxide groups and new polymer radicals in the *propagation reactions*. The hydroperoxide groups give alkoxy and hydroxyl radicals by photoinitiated or thermal splitting or energy transfer which causes accelerated degradation of the polymer chains. Since the most important photodegradation of polymers is initiated by sunlight in air, the mechanism of Bolland and Gee has become the basis for extensive studies of photodegradation and photostabilization during the last 40 years. The Bolland and Gee mechanism of photooxidative degradation has been verified by innumerable studies.

In addition to chain scission, the photolysis of a polymer in air gives a whole array of oxidized groups, e.g., carbonyl, hydroxyl, and carboxyl groups, and unsaturated groups, e.g., vinyl, vinylene and vinylidene groups, conjugated double bonds, etc. Some of these groups, e.g., ketones and unsaturated groups, absorb UV light quanta which cause further bond scission directly or by energy transfer to other labile groups. The ketone groups in an aliphatic chain are active and important as species for chain scission. After excitation by UV absorption, the CO groups in an alkane chain cause chain scission either by Norrish type I reaction to two chain end radicals and a CO molecule or Norrish type II reaction which involves disproportionation to one methyl and one vinyl end-group.

The chain termination reactions are due to radical combination to inactive products containing C—C bonds, stable peroxides, hydroxyl, and ketone groups. The common photostabilizers used are either UV absorbers or radical scavengers which react to prevent or retard degradation of the polymer.

Photodegradation of a polymer is usually related to sensitizers present in the form of *impurities* or *modified groups* which absorb light quanta, transfer the energy to other groups, and initiate polymer reactions. Commercial polymeric materials may contain such internal and external impurities from the manufacture, processing, and fabrication of a polymer to a polymeric material and from environmental exposure of the material [4].

ORGANIC COMPOUNDS AND OXYGEN

The *ground state of oxygen* is a triplet state which means that it contains two unpaired electrons and is chemically a biradical. As a result, molecular oxygen in the ground state cannot react directly with normal organic compounds containing electron pairs in all chemical bonds but only with free radicals which have unpaired electrons. This is the basis for the already mentioned photooxidative mechanism of photodegradation established by Bolland and Gee [3]. Molecular oxygen can also exist in *two excited states as singlet oxygen* containing electron pairs. One of these singlet states ($^1\Delta_g$) has an excitation energy of 22.6 kcal/mol and a lifetime of 45 minutes in the gas phase. The $^1\Delta_g$ state is formed, e.g., by UV irradiation of polluted air. It reacts easily with unsaturated groups in alkenes by direct addition of the excited oxygen molecule to hydroperoxide groups and with conjugated double bonds by cycloaddition to endoperoxides. These peroxides are further decomposed to other oxidized groups which also involves chain scission [5]. In this way, singlet oxygen is an initiator for photooxidative degradation of polymers, as recently reviewed by Clough et al. [6].

PHOTODEGRADATION OF SOME IMPORTANT POLYMERS

Cellulose and Synthetic Polyesters

The photodegradation and photooxidation of cellulose has recently been reviewed [7]. Cellulose in pure form has a UV absorption spectrum with a broad peak at about 265 nm and a second weaker peak at about 300 nm, forming a shoulder into the near-UV irradiation. These absorptions are assigned to the 1,4-glycosidic linkage between the anhydroglucose units in the cellulose chain (Fig. 1).

When pure cellulose is irradiated with UV light in N_2 atmosphere in a quartz tube at liquid N_2 temperature, four different radicals are identified in the ESR spectra: trapped hydrogen ($H\cdot$), formyl radical ($H\dot{C}O$), glycopyranose, and glycopyranose moiety radicals (Table 1). This means that hydrogen is abstracted and trapped in the sample and on the surface of the quartz tube. The sixth carbon atom group is split off, giving formyl radical ($H\dot{C}O$). Formaldehyde and hydrogen (H_2) are found in the off-gas evolved. The cellulose chain scission is shown in Fig. 1A. The photoinitiated chain degradation in air is faster than in N_2 or vacuum, and the cellulose is simultaneously oxidized. This is interpreted to mean that the peroxy radicals formed by oxygen addition to the chain-end radicals prevent the glycosidic bonds from reforming (Fig. 1B).

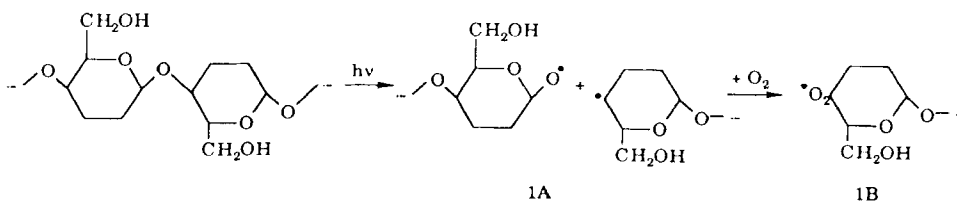


FIG. 1.

TABLE 1. ESR Spectral Studies of Free Radicals Formed in Purified Wood Cellulose, Irradiated with UV Light from a High-Pressure Mercury Lamp in Nitrogen Atmosphere at 77 K

ESR hyperfine coupling in Gauss	ESR spectral component	Identified radical structure
505	Doublet	$\text{H}\cdot$
130	Doublet	$\begin{array}{c} \text{HC}=\text{O} \\ \\ -\text{O} \end{array}$
25	Doublet	$\begin{array}{c} \text{HC}\cdot \\ / \quad \backslash \\ -\text{HC} \\ \\ \text{OH} \\ \\ \text{OH} \\ \\ \text{CH}- \\ \\ \text{O}-\text{CH} \\ / \quad \backslash \\ \text{CH}- \\ \\ \text{OH} \end{array}$
15 (width)	Singlet	$\begin{array}{c} \text{O}-\text{CH} \\ / \quad \backslash \\ \text{CH}- \\ \\ \text{OH} \end{array}$

When hydrogen and formyl radicals are split off, there are moiety radicals formed on the cellulose chains. These radicals give additional broad ESR spectral lines which so far have not been interpreted due to line overlap. Photolysis of xylan gives an analogous ESR spectrum but without indication of formyl radical formation, obviously because xylan has no sixth carbon atom group.

The photolysis of *aromatic polyesters* with UV irradiation, e.g., poly(ethylene terephthalate), is slow due to self-stabilizing effects. These polymers have absorption in the near-UV (300–400 nm) which causes degradation and rearrangements at

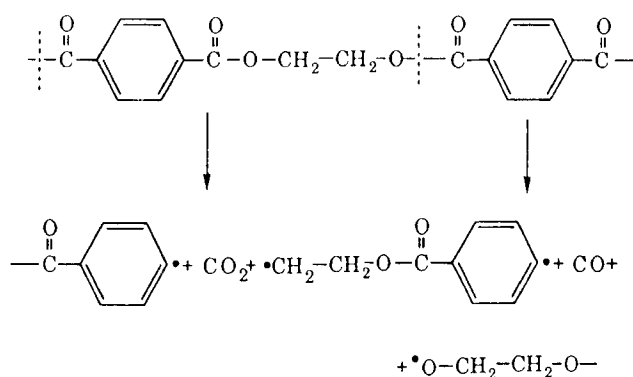


FIG. 2.

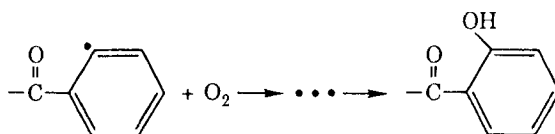


FIG. 3.

the surface, giving increased absorption, i.e., these reactions protect the bulk of the polyester. Some chain degradation occurs by splitting off CO and CO₂ groups [8]. At the same time the polymer surface is oxidized by molecular oxygen addition to the radicals formed, which further increases UV absorption (Fig. 2). Unsaturated polyesters, e.g., phthalic anhydride/maleic anhydride/ethylene glycol polymers, give ortho-hydroxybenzophenone structures as end groups when they are photolyzed (Fig. 3). Such groups are stabilizers because they absorb UV quanta and emit harmless radiation of longer wavelength. This surface layer is an efficient absorber of UV light and, therefore, a good photostabilizer for the unsaturated polyester [9]. To enhance the photostability, stabilizers have been grafted to polymer surfaces in research carried out in cooperation with Otto Vogl and his group.

Polyolefins and Diene Polymers

When irradiated with UV light of 300–400 nm in vacuum or in N₂ atmosphere at liquid N₂ temperature, *polyethylene* is a rather stable polymer. Irradiation with UV of short wavelength (254 nm) causes the formation of chain radicals by splitting off hydrogen and some chain-end radicals by chain scission (Fig. 4) identified by ESR spectra [10]. The hydrogen radicals are trapped on the inner surface of the ESR quartz tube. After prolonged irradiation, double bonds are formed by hydrogen abstraction (B) and identified as allyl radicals (C). Gradually, chain segments of polyenes are formed (D). The abstracted H[•] radicals abstract other hydrogens or combine to form H₂ molecules, which are identified by gas analysis. The chain radicals are formed in larger amounts than are the chain-end radicals (Fig. 4A). For

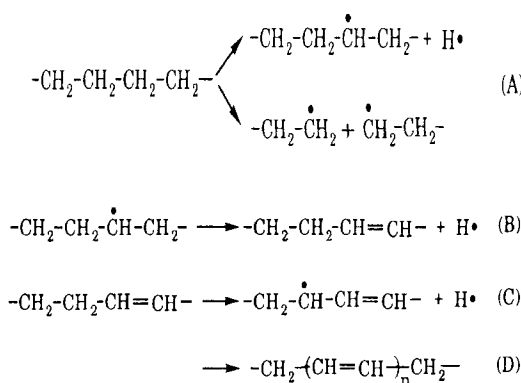


FIG. 4.

UV-irradiated polyethylene, crosslinking by chain and chain-end radical combination occurs at a higher rate than chain scission.

When oxygen is present during UV irradiation, e.g., exposure in air, a dominant reaction at the polymer surface is addition of molecular oxygen to the polymer radicals (Fig. 5). The peroxy radicals are reactive and abstract hydrogen from adjacent polymer chains. The resulting hydroperoxide groups decompose to alkoxy and hydroxyl radicals in the usual way. The alkoxy chain radical may abstract hydrogen to a hydroxyl group (Fig. 5A) or cause chain scission (Fig. 5B).

In the basic reactions of UV-irradiated *polypropylene* (PP), degradation occurs at a faster rate than does crosslinking. We discovered by our ESR studies in 1963 [11] that UV irradiation of PP in vacuum at liquid nitrogen temperature gave a broad-line spectrum of polymer radicals and a narrow-line quartet interpreted as due to methyl radicals (CH_3) (Fig. 6).

The mechanism of methyl radical formation was later interpreted as a reaction in several steps (Fig. 7). The first steps are abstraction of tertiary hydrogen, addition of oxygen, and formation of hydroperoxide groups. The splitting to alkoxy and hydroxyl radicals by energy transfer absorption of UV quanta would give methyl radicals and chain ketone groups, which by UV absorption breaks the chain by Norrish type I scission. This mechanism is supported by the ESR spectra and by gas analysis which shows carbon monoxide (CO) and methane (CH_4) as the main components of the gas evolved. Methyl radicals form methane by hydrogen abstraction. The methyl radical concentration is too low to give measurable amounts of ethane by methyl radical combination.

In a later study of the photodegradation of poly(isobutylene), small amounts of methyl radicals were found by ESR spectral analysis [12]. The mechanism is probably related to chain scission and is not resolved.

1,4-Polydienes are degraded with UV light by mechanisms studied with ESR spectroscopy by Carstensen in a series of papers [13]. The samples were purified polymers in quartz tubes, degassed and irradiated in vacuum at 77 K with medium pressure mercury lamps, giving main spectral lines from 254 to 365 nm. Three commercial polydienes were studied: polybutadiene, polyisoprene, and polychloro-

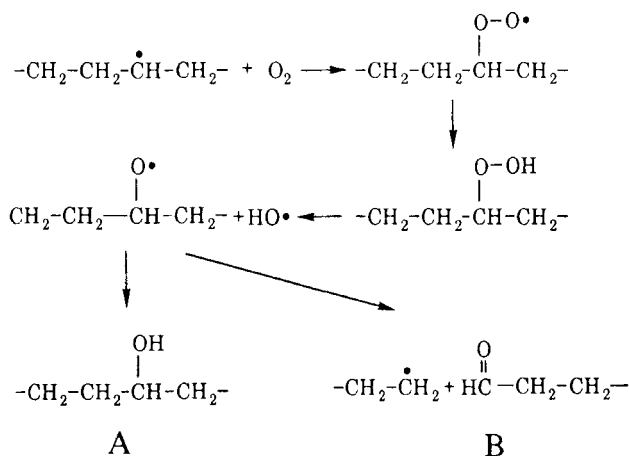


FIG. 5.

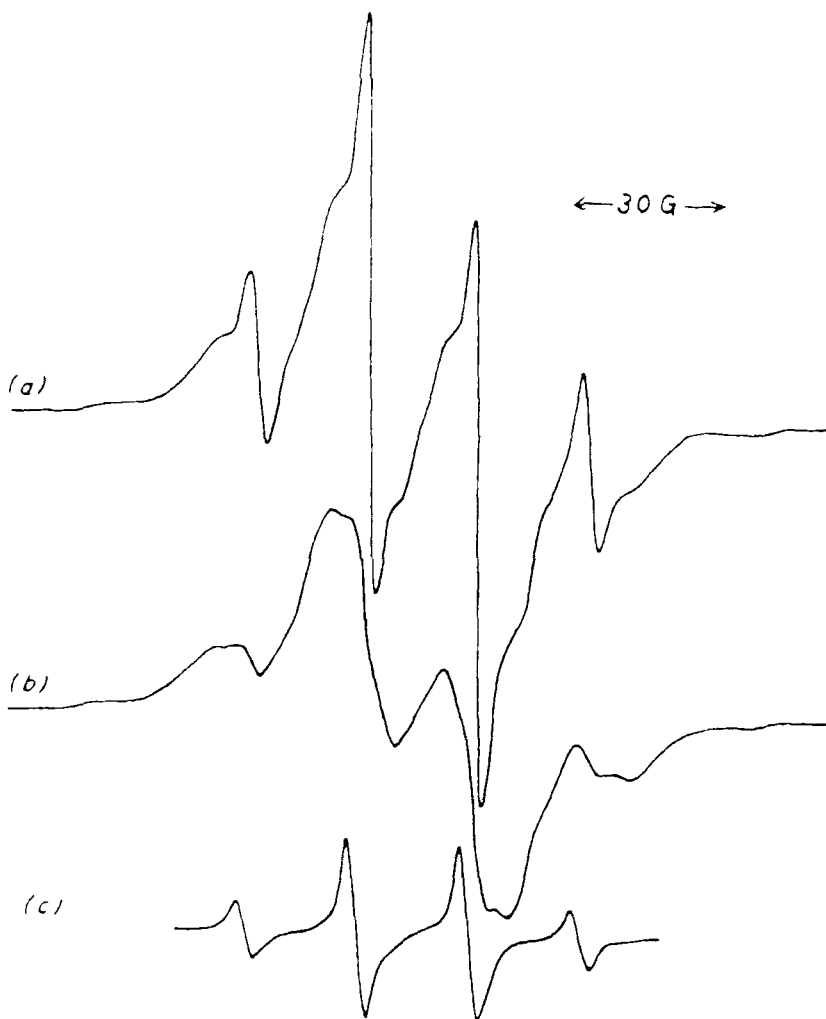


FIG. 6. ESR spectra of polypropylene irradiated with ultraviolet light at 77 K. Measurements at 77 K: (a) immediately after irradiation; (b) the sample as in (a) after being kept at 77 K for 2 days, the broad component of spectrum (a); (c) the spectral component which decayed during the first 2 hours at 77 K, the sharp component of spectrum (a).

prene. The ESR spectra for all three polydienes showed an even number of lines and were interpreted as due to allyl chain-end radicals formed by bond scission of the $\text{CH}_2\text{—CH}_2$ group in the polymer chain (Fig. 8). After a slight increase of the temperature from 77 to 114 K, the chain-end allyl radicals rearrange to another allyl radical which apparently is more stable (Fig. 8). This result is well in line with the known data for the C—C bond strength along the polydiene chains. The C—C bond midway between the double bonds is the weakest bond. The UV-initiated degradation of the three polydienes studied starts with $\text{CH}_2\text{—CH}_2$ bond scission in all cases. No gas evolution was found as a result of the degradation. The chain-end allyl radicals may rearrange to more stable allyl radicals (Fig. 8A).

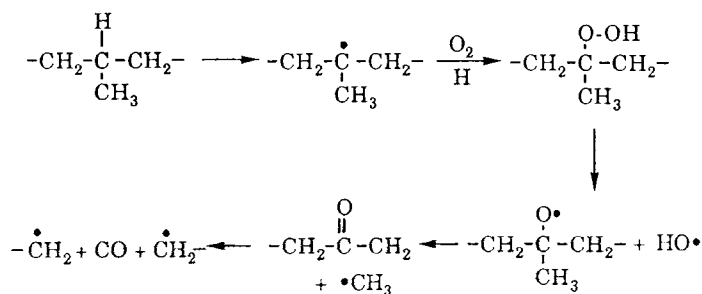


FIG. 7.

Polystyrene

Pure polystyrene (PS) without extraneous groups and analyzed in vacuum has no absorption in near-UV light, i.e., at 290 to 400 nm. It shows strong absorption at 250–280 nm due to the phenyl groups [14]. Commercial PS samples, radical polymerized under an oxygen-containing atmosphere, contain peroxide groups $-\text{O}-\text{O}-$ as chain elements. UV irradiation or heating breaks the weak $\text{O}-\text{O}$ bond (40 to 50 kcal/mol) and gives alkoxy chain-end radicals. Photoinitiated abstraction of tertiary-bonded hydrogens from the PS chains will occur preferentially, which initiates further oxidative degradation. Through the regular sequence of O_2 addition to chain radicals, hydrogen abstraction to hydroperoxide groups and $\text{O}-\text{OH}$ bond scission will give β -scission of the PS chain (Fig. 9A). The aromatic ketone groups increase absorption in the near-UV, and the $-\dot{\text{C}}\text{H}_2$ radical end groups cause further degradation, e.g., by abstraction of secondary-bonded hydrogen from $-\text{CH}_2-$ groups in the PS chains. The chain radical (Fig. 9B) may break the PS chain by disproportionation.

After bond scission in the PS chain, unzipping may occur upon heating, with the formation of styrene monomer to a yield of 40%. Processing of PS melt at temperatures of 180 to 200°C causes some chain scission and subsequent unzipping (Fig. 9C). This reaction is noticed from the smell of styrene monomer in a PS processing plant.

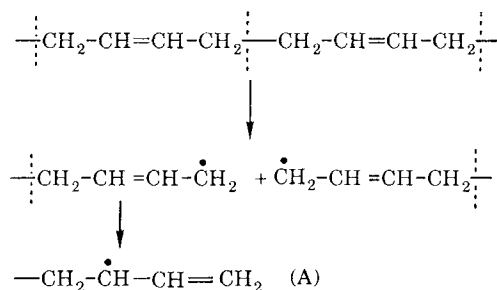


FIG. 8.

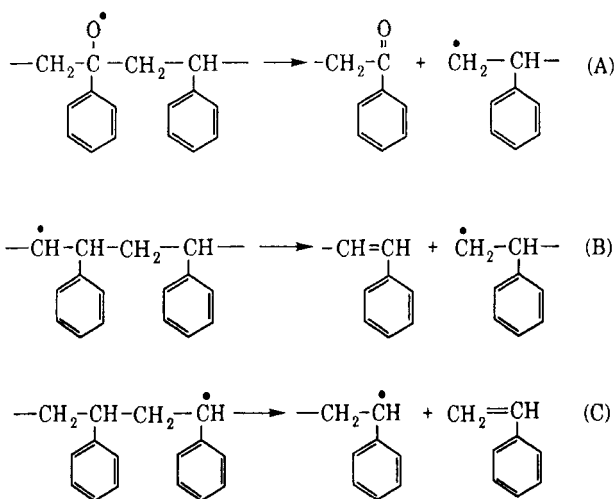


FIG. 9.

The photolysis of PS by sunlight in air causes a darkening of the polymer due to increased absorption near 400 nm, i.e., of blue light. The appearance of dark color is interpreted as due to an oxidative ring-opening reaction of the phenyl groups with O₂ to mucondialdehyde groups (Fig. 10) [15]. This reaction is preceded by formation of an O₂ complex with the excited phenyl groups. A possible intermediate is an endoperoxide formed by addition of singlet oxygen to the phenyl group. The reactions in Fig. 10 are verified by model experiments with benzene, photolyzed with oxygen, forming *trans-trans*-2,4-hexadiene-1,6-dial (mucondialdehyde) and other conjugated structures. Other degradation reactions, e.g., quinone formation, are also proposed for the oxidative photolysis of polystyrene. The degraded and

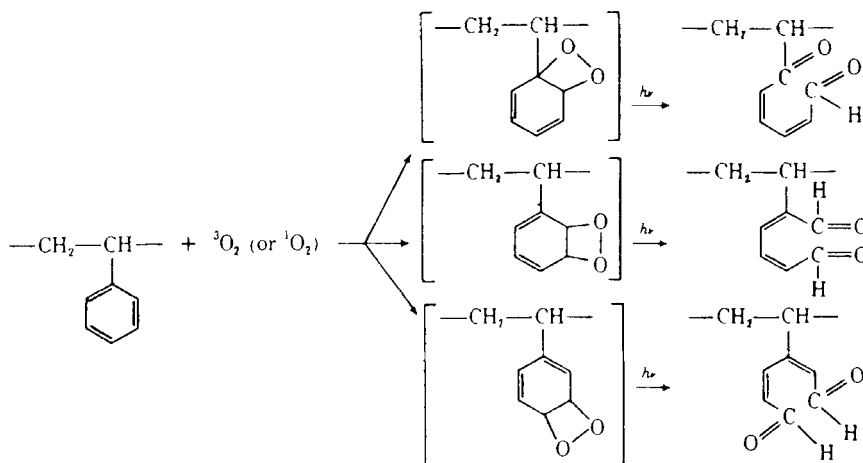


FIG. 10.

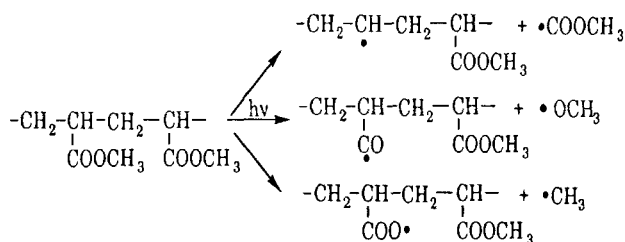


FIG. 11.

oxidized polymer contains several absorbing groups for UV and visible light, which causes discoloration and increasing brittleness.

Polyacrylates and Polymethacrylates

Poly(methyl acrylate) and poly(ethyl acrylate) are important polymers in surface coatings and adhesives. The absorption in near-UV is very low but increases gradually during photolysis, indicating carbonyl group formation. At the same time, formaldehyde, methanol, and methyl formate and also carbon monoxide, methane, and hydrogen are evolved as volatile products. The main reactions are interpreted to be bond scissions in the side group (Fig. 11). The three reactions shown give split-off radicals which, after hydrogen abstraction, e.g., of tertiary-bonded hydrogen, produce three of the volatile products analyzed: methyl formate,

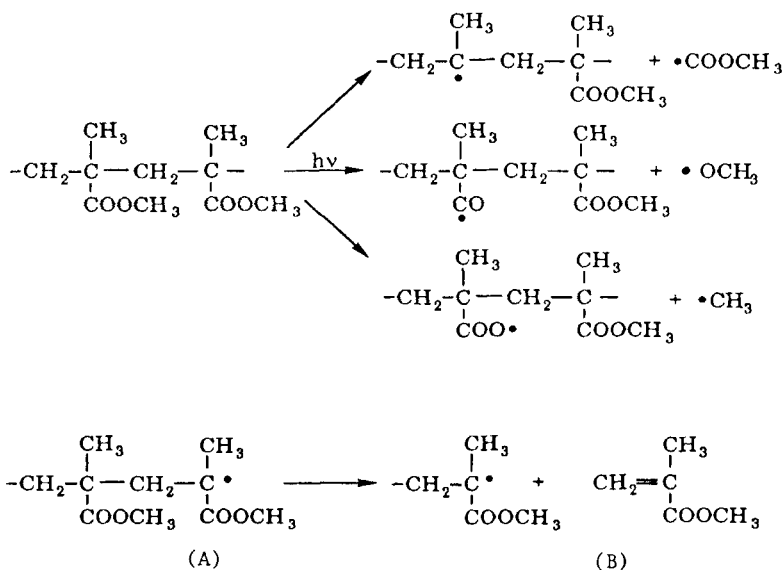


FIG. 12.

methanol, and methane, respectively. The chain radicals may combine to form crosslinks which is a more rapid reaction than chain scission in vacuum or inert gas.

Poly(methyl methacrylate) (PMMA) also has very low absorption in near-UV light and is, therefore, largely transparent to the whole spectrum of sunlight. The photolysis is primarily related to bond scission in the side groups as described for poly(methyl acrylate) (Fig. 12). The same volatile compounds are also formed. The difference between PMMA and PMA in photodegradation is mainly related to the tertiary-bonded methyl groups in PMMA which are not as easily abstracted as tertiary-bonded hydrogens [16]. UV irradiation of PMMA initiates some random chain scission (Fig. 12A) and subsequent unzipping of methyl methacrylate monomer (Fig. 12B). This is not very serious for the mechanical stability of the PMMA material because the radical pairs may combine again. In addition, the monomer formed is compatible with the polymer and gives only some local plasticizing. This explains why PMMA is a highly photostable and transparent polymer which can be used as window panes and light domes in building constructions.

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