Biodegradability of Photooxidized Polyalkylenes

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Synopsis

Representative polyolefin films were exposed to UV radiation from light sources having different intensities and spectral distribution including the quartz mercury arc, fluorescent lamps, xenon arc, and sunlight. Films exposed were polyethylene, polypropylene, and sensitized polyethylene. The oligomer fractions were separated from the high polymer and were challenged microbiologically. The oligomer fractions supported microbial growth, but the high polymers gave minimal or no growth. It was concluded that photooxidative degradation of polyolefins does not per se induce progressive attack by microorganisms. Oligomers present originally in the polymer are augmented by those produced by photooxidation. These oligomers support growth if separated from the polymer matrix. These observations explain some of the contradictory reports in the literature concerning the microbial degradation of sensitized polyolefins.

INTRODUCTION

The conditions under which organic polymers are removed from the environment and their components reintroduced into the various biological cycles are of ecological interest. Many natural polymers such as those based on cellulose or protein are susceptible to microbial attack. Under favorable conditions such as high humidity or burial in microbially active soil, they undergo rapid attack and are ultimately mineralized.

On the other hand, high molecular weight synthetic polymers as a class are resistant to biodegradation.[1] The only important exceptions are polymers with aliphatic esters in the main chain and polyurethanes based on polyester diols.[2-4]

Polycaprolactones of various molecular weights were reported to have undergone complete hydrolysis and metabolism by a number of fungal species which were able to use them as sole carbon sources.[5] Pure bacterial cultures and a yeast degraded polycaprolactone but not as effectively as a mixed culture.[6] The mechanisms of polycaprolactone biodegradation by fungi[7] and by enzymes[8] has been studied turbidimetrically and by the scanning electron microscope. Another major route for polymer degradation in the biosphere involves initial interaction of the polymer with environmental forces such as light and oxygen. This photooxidative process results in the formation of smaller fragments whose chemical and physical properties are different than the original polymer. It has been claimed that these fragments now can be readily attacked by microorganisms and thus be reintroduced into the various biocycles.

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The polyalkylenes (e.g., polyethylene, polypropylene) are difficult to degrade because the unmodified polymer is resistant to attack either by microorganisms or by chemical means other than photooxidation. A saturated hydrocarbon of this type would be expected to absorb energy only in the vacuum ultraviolet (less than 200 nm). However, impurities introduced during fabrication render most polymers vulnerable to photolytic change to some extent under ambient conditions.

In polymers which are to be made photodegradable it is necessary to increase the sensitivity to light in a controlled manner. Generally such photosensitized polymers are employed for disposable plastic films or containers. After discarding out-of-doors, they are expected to disintegrate after some predetermined period under average environmental conditions. Obviously it is vital that the integrity of the container not be compromised by premature damage under the conditions of storage prior to use. On the other hand, it is desirable that the packaging material disappear as rapidly as possible once it has been discarded.

In an attempt to meet these contradictory requirements a number of workers have proposed different methods to enhance the photodegradability of plastic films or containers. Guillet[9] has introduced several light sensitized polymers under the general name Ecolyte.

In this type of polymer, carbonyl groups which are introduced adjacent to the main chain, absorb UV light and bring about cleavage of the chain. Quantum yields are dependent on the structure of the absorbing group and the chain length.[10] The light sensitizing component is chemically bonded to the polymer and therefore cannot be lost by migration.

Scott[11] introduced the use of antioxidants such as the ferric dialkylthiocarbamates as delayed action photosensitizers. On irradiation these complexes act first as UV stabilizers but after an induction period become accelerants for polymer decomposition. It has been shown[12] that the antioxidant effect is the result of the formation of a Lewis acid which catalyzes the cleavage of hydroperoxides. The useful life of the film or container can be adjusted by varying the initial concentration of the antioxidant.[12,13]

After a period of irradiation the photosensitized polymer undergoes a reduction in molecular weight and becomes brittle. The action of mechanical forces of the biosphere such as wind or water cause it to crumble to a fine powder, which may be dispersed with and is almost indistinguishable from the surrounding soil. It has been claimed that polyalkylenes photodegraded in this way undergo biological oxidation because of the reduction in molecular weight and particle size.[14]

The objective of the present research is to investigate the photooxidative decomposition of several different types of polyalkylenes and the susceptibility of the products to further attack by microorganisms. The polymers studied were: polypropylene (PP), high density polyethylene (PE), and sensitized polyethylene (SPE). The extent of photolytic decomposition of these materials under a variety of light sources of differing spectral distribution and intensity was studied. The nature of the chemical species produced was examined. The susceptibility of these products to microbiological attack was determined and is of interest in predicting the extent to which these polymers can indeed undergo biodegradation subsequent to photolytic attack.

EXPERIMENTAL

Methods

All irradiation was carried out in a closed hood with a strong air current to insure removal of ozone and volatiles. Weights were obtained with a standard Mettler analytical balance. All solvents used in this study were of the highest quality purchased from Burdick and Jackson.

Materials

Sensitized Polyethylene (SPE). Natural mulch film, 1.5 mil thickness, supplied by Arco Polymers, Inc., 7001 W. 60th St., Chicago.

Polyethylene (PE). Virgin high density film, 2.0 mil thickness supplied by General Equipment and Packaging Laboratory, Natick Labs.

Polypropylene (PP). Virgin 2.5 mil film, supplied by General Equipment and Packaging Laboratory, Natick Labs.

Irradiation. Samples were irradiated with a 550-watt Hanovia High Pressure quartz mercury vapor light source (6515-16), used without reflector, at 30.5 cm from the sample. Based on the manufacturer's data, the total radiant UV flux impinging on the sample is estimated to be 10.13 milliwatts/cm.

Photodegradation—Determination of Volatiles. Sample discs 45 mm in diameter were prepared and weighed in tared 55-mm diameter aluminum weighing cups. Each cup was placed in the bottom of a 400-mL beaker, and the samples exposed simultaneously to the UV source placed in the horizontal position at a distance of 30.5 cm. The degradation was conducted in an efficiently ventilated hood, and the samples were further protected from disturbance due to the air current by a suitable baffle. The ambient temperature in the vicinity of the sample reached 35°C. Samples were periodically weighed, and the weight loss determined. An aluminum cup with no polymer underwent no significant change in weight when irradiated concurrently.

Photodegradation—Determination of Soluble (Intermediate) Fraction. Three sheets of SPE were attached to cardboard frames (exposed area 19.5 × 24.5 cm) and exposed to the UV lamp mounted on the vertical position. The configuration was such that the lamp was surrounded on three sides by the sheets hung vertically at a distance of 31 cm. At the end of 65 h, the samples had totally shredded. The fragments were removed from the frames, combined, and spread as a thin layer on a Pyrex dish. The irradiation was continued with the lamp horizontal at the same distance. The polymer layer was occasionally stirred to expose new surfaces. At intervals, accurately weighed samples (1.0–1.5 g) were taken and extracted with 50 mL of THF for 8 h with gentle agitation in a glass-stoppered 250-mL flask. The supernatant was separated by filtration. The soluble fraction was evaporated to constant weight *in vacuo*, and the weight of the residue (soluble fraction) determined.

Other Sources. In addition to the quartz mercury arc other light sources were used having different spectral characteristics or exposure conditions. A QUV Accelerated Weathering Tester, Q-Panel Company, Cleveland, OH,

was used to expose sheets of polyolefine films with continuous fluorescent illumination, at 65 ± 2°C without cycles of water condensation. Polyethylene, sensitized polyethylene, and polypropylene were exposed for 100, 150, 200, and 300 h. The polypropylene and sensitized polyethylene began to shred after 250 h of exposure and were removed. The films were extracted and the oligomers obtained in this way were characterized by their IR spectra.

Xenon arc exposures were carried out with an Atlas Ci35W Weather-Ometer, Atlas Co., Chicago. Continuous illumination was employed with no water spray cycle. The irradiance was 0.55 W/m^2 (340 nm calibration), the black panel temperature was 63°C, and the relative humidity 60%. The films were exposed for 200, 300, and 400 h. After the 400-h exposure only the polyethylene remained intact, the other polymers having disintegrated. The oligomers were obtained by extraction with THF and characterized by IR spectroscopy.

The outdoor exposures were conducted in Hudson, Mass., at the U. S. Army Natick Research and Development Laboratories facilities. The samples were tacked on open-backed wooden racks and exposed in an unshaded area facing south at a 45° angle. The exposure period was for 6 months (5 May 1980–31 October 1980) and data for the period are collected in Table I.

TABLE I
Climatological Data during Outdoor Exposure Period[a]

Receptor	Radiation intensity (J/m^2 × 10^4) May 1980	June 1980	July 1980	Aug 1980	Sept 1980	Oct 1980
Sel. wave[b] Clear[c]	55,700	56,285	63,675	51,295	59,660	49,265
Sel. wave lt. yel.[d]	49,510	50,155	57,310	46,870	55,865	45,350
Sel. wave yet. or.[e]	38,125	38,405	43,265	35,540	54,010	35,895
Sel. wave lt. red[f]	30,705	29,630	34,315	27,455	32,930	28,330
Sel. wave dk. red[g]	25,190	25,255	29,285	24,155	29,510	25,185
N.I.[h] Clear[c]	48,580	53,615	52,000	45,650	53,060	43,725
N.I. lt. yel.[d]	42,435	46,610	45,685	31,740	45,755	38,035
N.I. yet. or.[e]	36,330	39,985	38,960	26,960	39,510	32,665
N.I. lt. red[f]	30,900	34,105	32,465	22,610	33,470	27,445
N.I. dk. red[g]	24,150	26,570	26,385	18,795	27,245	22,470
Vert. Eppley[c]	59,415	64,380	70,385	53,120	50,170	46,830
45° reflected[c,i]	11,865	12,395	13,340	10,310	9810	7005
Temp (°C) monthly av.	14.2	17.2	22.5	21.6	16.8	8.5
Rel. humidity (%) monthly av.	63	70	70	74	70	70

[a] Data obtained by U. S. Army Meteorological Team at Natick Labs Annex, Sudbury, Mass.
[b] Sel. wave = selective wave, sensor oriented south at 45° inclination.
[c] Window 280 nm to 3.3 μm.
[d] Window 395 nm to 3.3 μm.
[e] Window 530 nm to 3.3 μm.
[f] Window 620 nm to 3.3 μm.
[g] Window 700 nm to 3.3 μm.
[h] N.I.; normal incidence, sensor oriented normal to sun.
[i] Oriented N at 45° inclination.

Gel Permeation Chromatography (GPC). GPC was carried out with a Waters 150 C High Temperature Chromatograph using trichlorobenzene (TCB) at 140°C as mobile phase with four Porogel columns in tandem. Molecular weight parameters were computed using a Waters Data Module with GPC capability.

GPC was also performed by Springborn Laboratories, Enfield, Ct., using a Waters 200 chromatograph with TCB at 140°C at a flow rate of 1 mL/min with 5 Styrogel columns in tandem, (10^7, 3×10^6, 10^5, 10^3 Å).

Gas Chromatography/Mass Spectrometry (GC/MS). GC/MS was carried out with a Finnigan MS with capillary columns programmed from 40°C to 350°C.

Microbiological Testing. The irradiated polymers and fractions were evaluated for their ability to support fungal growth using the standard ASTM G21 method[15] modified in the following manner: in addition to the test fungi cited in the ASTM G21 method, spores of *Aspergillus versicolor,* QM432 and *Aspergillus flavus,* QM380 were also added to the mixed fungus spore suspension. Instead of using an atomizer to ionoculate the surface of the test specimens, three drops of the spore suspension were added to each Petri dish followed by adding warm ASTM nutrient salts agar to the dishes with swirling. The test specimens (130 ± 5 mg) were then added aseptically to the surface of the inoculated hardened agar and incubated at 30°C for 8 weeks with appropriate controls. In addition, since the various polymers evaluated are of hydrocarbon origin, they were also evaluated against the fuel-utilizing fungus *Cladosporium resinae,* QM7998 in Bushnell and Haas[16] mineral salts broth and agar using the procedure previously described.

The photolyzed polymers were extracted and the oligomeric fraction examined by IR spectrometry. The spectra of the oligomers from each polymer type, e.g., SPE, were qualitatively similar irrespective of the light source used. All of the oligomers exhibited bands that indicated the presence of carbonyl and hydroxyl groups in addition to the expected hydrocarbon bands.

RESULTS AND DISCUSSION

Commercial samples of virgin polypropylene (PP), polyethylene (PE), and sensitized polyethylene (SPE) were exposed to UV radiation under physical conditions which are qualitatively similar to those met in the environment, that is, freely circulating air and ambient conditions of temperature and humidity. The production of volatiles, determined by the loss of weight of the exposed samples, is presented in Figure 1.

Polypropylene underwent a rapid photolysis, almost 90% having disappeared after 440 h exposure. SPE and PE degraded less rapidly than PP. The SPE also lost mechanical strength and shredded after about 60 h exposure. However, after 200 h SPE and PE appeared to lose weight at about the same rate.

It is reasonable to suppose that the volatiles from PE consist largely of low molecular weight fragments. It has been shown that linear hydrocarbons of molecular weight less than 450 support microbial growth.[17] It is probable that most of the linear volatile products from PE or SPE would

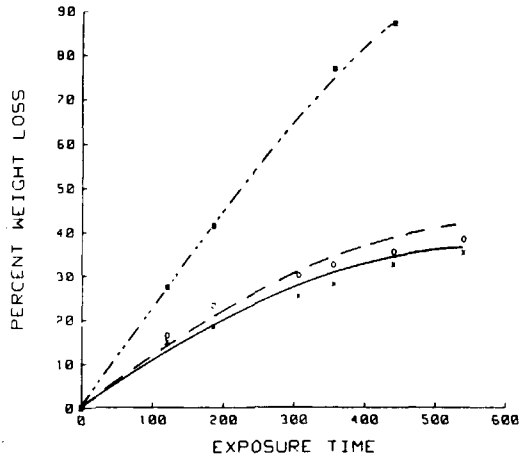

Fig. 1. Weight loss of polyalkylene films vs. hours of exposure to 550-W quartz mercury arc in air; PE, polyethylene (——), SPE, sensitized polyethylene (– – –), and PP, polypropylene (– · · –).

be ultimately degraded by environmental factors in the biosphere. In the case of PP the products should contain highly branched hydrocarbon molecules. The fate of these volatiles cannot be assumed, since branched chain hydrocarbons of molecular weight as low as 200 did not support growth.[17]

It was also of interest to examine the oligomers (nonvolatile products of low molecular weight) formed by photodegradation of the polymer. Since high molecular weight polyethylene is virtually insoluble at room temperature, the oligomer fraction was obtained by solvent extraction at room temperature (Fig. 2).

A plot of the oligomer fraction as a function of exposure time is shown in Figure 3. From an initial value of 5% in the unirradiated polymer this

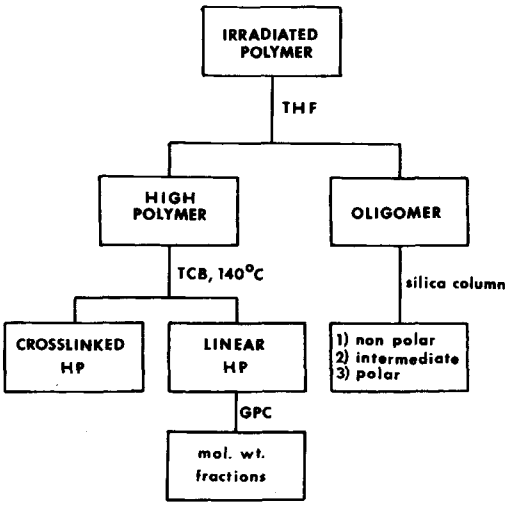

Fig. 2. Scheme for the separation and characterization of fractions from irradiated polyolefin films: THF, tetrahydrofuran; TCB, trichlorobenzene; HP, high polymer; GPC, gel permeation chromatography.

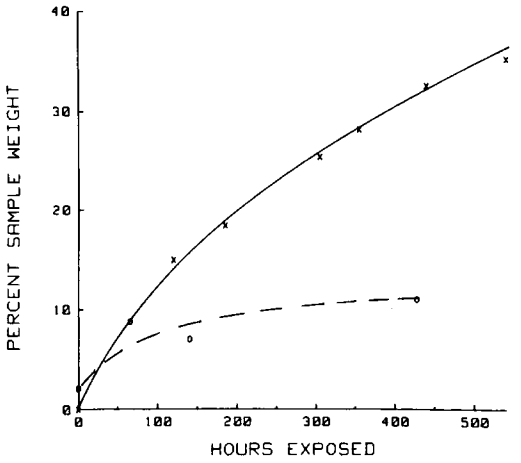

Fig. 3. Formation of volatiles and tetrahydrofuran (THF) soluble fractions on exposure of SPE to quartz mercury arc in air: (——) % volatile; (---) % soluble.

fraction approached a value of about 10% after lengthy exposure. The volatile fraction was concurrently produced at a greater rate, as shown by the upper curve of the same igure.

These results suggest that SPE undergoes an initial rapid photodecomposition which results in loss of strength, the production of a soluble oligomer fraction, and a volatile low molecular weight fraction. Adams[18] has reported the production of oligomers by photolytic and thermal stressing of ordinary PE and PP.

The photolyzed SPE samples were further fractionated as shown in Figure 2. Since the linear high polymer is soluble in trichlorobenzene at 150°C while the crosslinked polymer is not, it is possible to determine the amount of crosslinked fraction gravimetrically.

The average molecular weight ($\overline{M}_N$) of the irradiated SPE was determined by gel permeation chromatography after removal of the crosslinked and oligomer fractions. A plot of $\overline{M}_N$ of the soluble fraction and wt % of crosslinked fraction as a function of exposure time is shown in Figure 4. The rapid decrease in $\overline{M}_N$ of the SPE on exposure to UV is accompanied by an increase in the concentration of the crosslinked fraction.

Since a relatively high proportion of the polymer is volatilized, it is instructive to recalculate the amount of each fraction as a percent of the original sample weight taking into account this loss. A plot of these parameters as a function of exposure time is shown in Figure 5.

The oligomer portion soluble in THF at room temperature constitutes less than 5% of the unexposed polymer. It increases to a limiting value of about 9% after exposure, but does not appear to increase upon further irradiation.

These results suggest that SPE undergoes an initial rapid photodecomposition which results in a large reduction of the average MW and loss of mechanical strength. As a result of this process, a soluble oligomer fraction and a low MW volatile fraction are formed. Continued irradiation appears to result in a steady state situation in which about as much of the oligomer

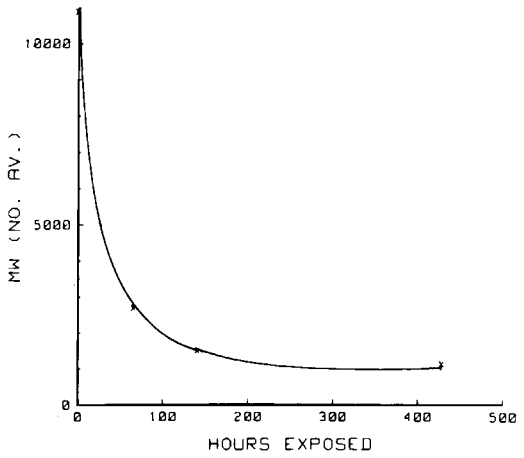

Fig. 4. Number average molecular weight (M_N) of SPE vs. hours of exposure to quartz mercury arc in air.

is cleaved and volatilized as it is formed. Thus, this fraction approaches a quasiequilibrium value while the polymer as a whole is being photodegraded. After its original rapid formation the crosslinked fraction undergoes a slow buildup. Figure 6 is a schematic showing the relationships of these fractions.

Figure 7 is an IR scan of the oligomer that was extracted from irradiated sensitized PE. The band at 3450 cm^{-1} indicates the possibility of an —OH group, possibly from an acid or an alcohol. In addition to bands due to CH stretching and bending, the absorption in the 1700–1800 cm^{-1} area is probably due to carbonyl functions from a number of different compounds such as acids, esters, or ketones. Figure 8 is a scan of the extract from nonirradiated SPE, and even in this case there is evidence for the presence of a small number of these carbonyl groups, although the absorption is not as strong as in the irradiated sample. A small amount of carbonyl-containing oligomer is also present in nonirradiated ordinary PE.

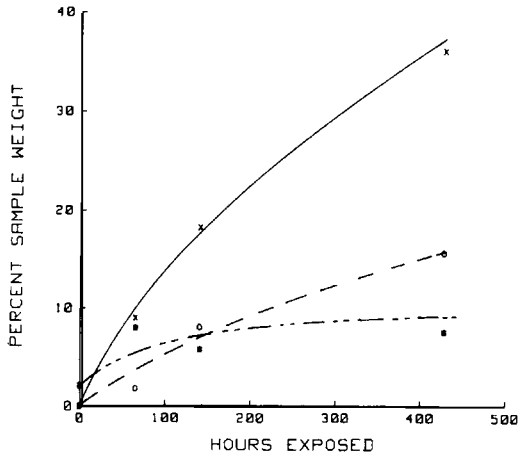

Fig. 5. Formation of volatile (——), oligomer (tetrahydrofuran soluble) (– · · –), and crosslinked (trichlorobenzene insoluble) (– – –) fractions from SPE on exposure to quartz mercury arc in air.

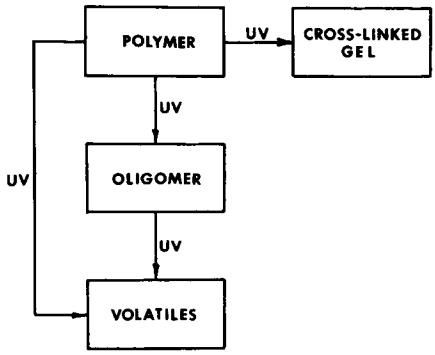

Fig. 6. Proposed scheme for the formation of crosslinked, oligomer, and volatile fractions on UV irradiation of polyolefins.

The oligomer from irradiated SPE was separated by chromatography on a silica gel column using methylene chloride as eluant. The polarity was gradually increased to obtain the various fractions in order of their polarity. Three main fractions were obtained; a nonpolar fraction which emerged first, an intermediate fraction, and a polar fraction which was last to elute.

The IR spectrum of the nonpolar fraction was essentially that of a saturated aliphatic hydrocarbon. In addition to these bands, the intermediate fraction exhibited a strong absorption at 3450 cm^{-1} with weaker absorptions at 1650 cm^{-1}, probably due to the presence of carbon to carbon double bonds and at 1730 cm^{-1}, due to carbonyl, e.g., carboxylic acid, ester, aldehyde, or ketone.

The polar fraction, which was the most highly retained, exhibited a prominent broad carbonyl bond at 1730 cm^{-1}. The bands resulting from saturated hydrocarbon absorption were present, but that the 3450 cm^{-1} band thought to be due to —OH in the intermediate fraction was greatly reduced.

These results can be rationalized on the basis of the structure of SPE, which is a linear polymer consisting of methylene groups with ketone groups

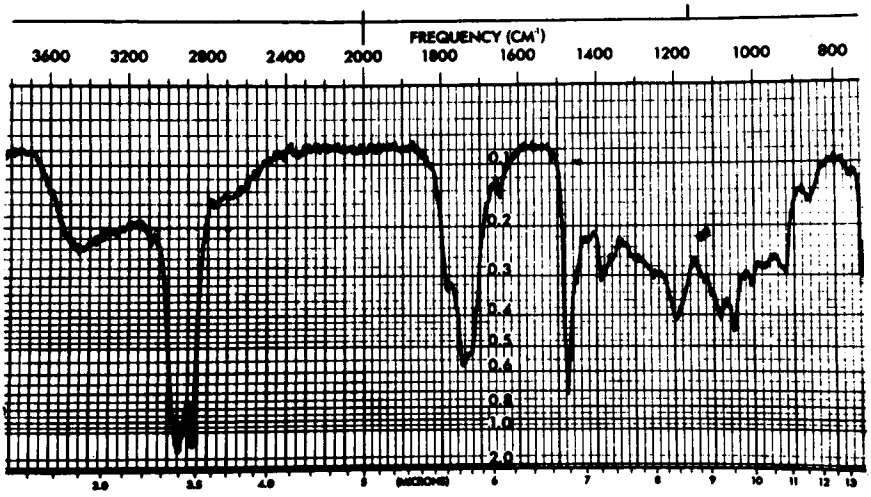

Fig. 7. IR scan of oligomer extracted from SPE irradiated for 130 h by quartz mercury arc in air.

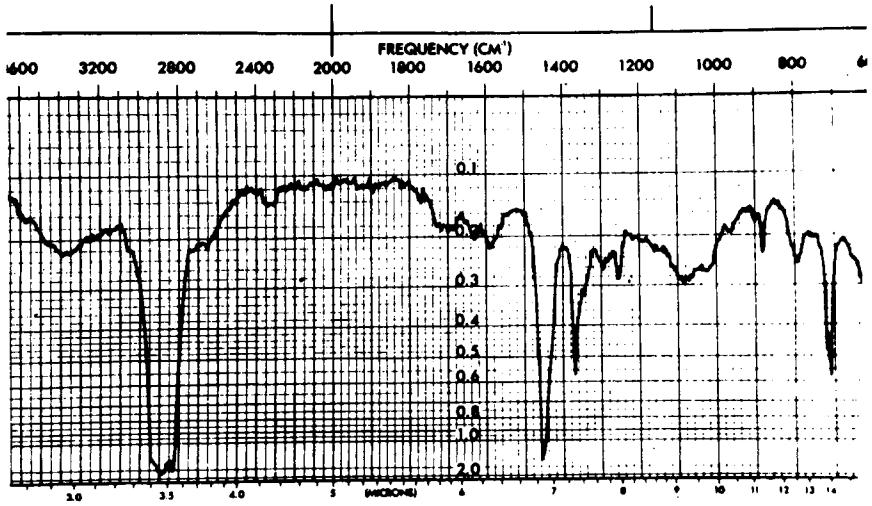

Fig. 8. IR scan of oligomer extracted from nonirradiated SPE.

pendent to the main chain (Fig. 9). These absorb light energy and then undergo Norrish type I and type II decomposition. Type I leads simply to the formation of two radicals, but does not result in cleavage of the polymer backbone. Type II results in the immediate cleavage of the main polymer chain leading to the formation of a ketone and an olefin. The radicals resulting from the type I decomposition may react with molecular oxygen giving rise to peroxides and hydroperoxides in a manner similar to the known chain reaction scheme for the auto oxidation of saturated hydrocarbons.[19]

In the case of polypropylene it has been shown that polypropylene hydroperoxide decomposes by homolytic cleavage to give a radical and a ketone, or it can undergo a second type of decomposition to give an alcohol.[20]

On the basis of the known photochemistry of aliphatic ketones, the autooxidation of saturated hydrocarbons, and the decomposition processes of aliphatic peroxides the finding of hydroxyl and carbonyl groups in the oligomer fraction from SPE is reasonable.

Chromatographic analysis of the oligomer fractions from irradiated PE and PP gave a similar product profile to that of SPE. This is not unexpected since the photoxidative attack is initiated by carbonyl impurities in every case and the mechanism is similar. Oligomer samples from PE films which

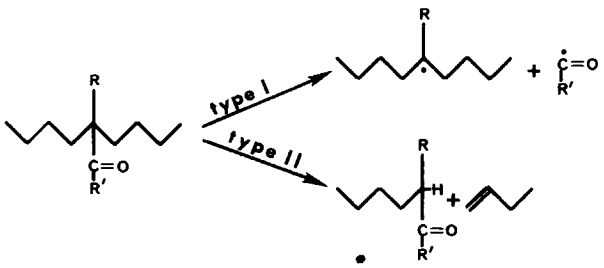

Fig. 9. Scheme for photodecomposition of sensitized polyalkylenes via Norrish type cleavage.

had been exposed for 88 and 143 h to radiation from fluorescent lamps in an accelerated (QUV) tester were analyzed by capillary GC/MS. Both samples exhibited a series of 17 major distinct peaks representing aliphatic hydrocarbons from C-16 to C-32. Each major peak could be further resolved by selected ion monitoring into a saturated (m/z 43, 57) and an olefinic (m/z 55, 69) component. The ratio of the saturated to olefinic components was estimated to be 2.5:1 based on the total ion current. The oligomers were separated into nonpolar, intermediate and polar fractions by chromatography on silica gel. The GC/MS analysis of the nonpolar fraction gave 29 peaks representing aliphatic hydrocarbons from C-15 to C-43. Attempted analysis of the other fractions did not give any defined peaks.

These results are consistent with the structure of SPE and the mode of photochemical cleavage proposed for it (Fig. 9). Type II cleavage and subsequent photooxidation of the primary products would account for the olefinic, carbonyl, and the hydroxyl groups found in the oligomer. On the other hand, the photodecomposition of PE and PP is probably initiated by the presence of oxygenated groups of various types randomly introduced in the polymer during thermal processing.

SPE, PE, and PP films were exposed to different light sources, e.g., mercury arc, fluorescent lamps (QUV tester), the xenon arc, and sunlight. Each of the first three sources emits a smaller component of short-wave UV radiation in the order named. The xenon arc and the sun have a similar distribution of spectral energy, but exposures to sunlight are necessarily intermittent and may be affected by other environmental factors.

The fractions obtained by extraction of the polymer films which had been exposed for various periods were subjected to microbial challenge using the ASTM spore mixture as inoculum. The experiments were repeated with *Cladosporium resinae* as inoculum and growth was rated on a scale of 0 (no growth) to 4 (heavy growth).

Table II shows the results of microbial challenge of EPE fractions which had been irradiated for up to 430 h by the quartz mercury arc. The samples are the irradiated high polymer fractions which had been extracted with THF but were insoluble. They thus included insoluble linear high polymer and crosslinked polymer, but the soluble oligomer had already been removed by THF. Nonirradiated PE and PP were introduced as controls, and gave minimal growth. With cotton and leather as positive controls, heavy growth was obtained. The Bushnell–Haas control gave about the same growth as the EPE fractions. It was concluded that the high polymer fractions, even after extensive irradiation and reduction in molecular weight gave minimal excess growth over the controls.

A modified scheme for fractionation which was adapted to obtain larger quantities of the various fractions needed for microbiological tests is shown in Figure 10. The irradiated polymer was successively extracted with methanol and then with dichloromethane, thus giving a series of soluble fractions of increasing polarity and an insoluble nonpolar fraction.

The results of microbial challenge of SPE fractions employing dichloromethane as extractant are given in Table III. Unexposed SPE and a sample which had been exposed for 150 h to the quartz mercury arc were employed. Neither exposed or nonexposed high polymer (insoluble) fractions supported

TABLE II
Microbial Growth on Polymers

Substrate	Exposure[a] (h)	M_N	% Crosslinked	Growth[b] ASTM[c] BHB[e]	ASTM[c] BHA[f]	*C. resinae*[d] BHB	*C. resinae*[d] BHA
SPE[g]	0	10,980	0	0	+	+	—
SPE	65	2695	2.2	+	+	+	+
SPE	140	1507	10.6	+	+	+	+
SPE	428	1133	27.8	+	+	+	+
PP[h]	0	—	—	+	+	+	+
PP	0	—	—	+	+	+	+
Cotton	0			++++	++++	—	++++
Leather	0			++++	++++	—	++++
BH control[i]	—			+	+	+	—

[a] Mercury arc.
[b] After 80 h (+ slight, ++ moderate, +++ good, ++++ heavy growth).
[c] ASTM fungal spore mixture inoculum.
[d] *C. resinae* inoculum.
[e] Bushnell–Haas broth.
[f] Bushnell–Haas agar.
[g] SPE = sensitized polyethylene.
[h] PP = polypropylene.
[i] BH = Bushnell–Haas.

any substantial growth. The successive fractions from the dichloromethane extraction did give growth on BH agar, but later fractions gave less growth. With the ASTM media no growth was obtained on the high polymer, and the extracts gave some growth, but the pattern of decreasing growth with successive extracts was not observed with this medium.

Microbial challenge of PE fractions which were obtained from irradiated and nonirradiated samples using THF as extractant is shown in Table IV. High polymer (insoluble) which had been freed of oligomer by extraction failed to support any growth, but unextracted exposed high polymer gave minimal growth. The oligomer fractions did support growth, but fractions obtained from the second and third extractions supported lighter growth than the first extraction. In this case ASTM media and BH agar exhibited the same pattern of growth.

Table V shows the results of a similar experiment with PP as substrate. Since this polymer is more UV sensitive than either PE or SPE, only 75 h

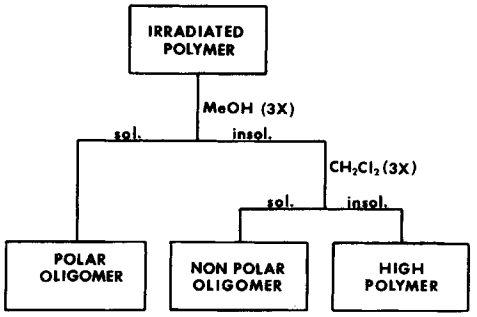

Fig. 10. Scheme for isolation of larger quantities of irradiated polyalkylene fractions by solvent extraction.

TABLE III
Microbial Growth on Fractions Extracted from SPE

Exposure[a] (h)	Solubility[b]	Solvent[c]	Microbial growth[d] ASTM[e]	Microbial growth[d] BH agar[f]
150	i	CH_2Cl_2	0	+
150	s	1st CH_2Cl_2	—[g]	—[g]
150	s	2nd CH_2Cl_2	++	++++
150	s	3rd CH_2Cl_2	+	++
0	i	CH_2Cl_2	0	0
0	s	1st CH_2Cl_2	0	+++
0	s	2nd CH_2Cl_2	+	++
0	s	3rd CH_2Cl_2	+	+
0	s	1st CH_2Cl_2[h]	+	+++

[a] Mercury arc.
[b] i = insoluble, s = soluble.
[c] First CH_2Cl_2 = first extract with dichloromethene, etc.
[d] + slight, ++ moderate, +++ good, ++++ heavy growth.
[e] ASTM fungal spore mixture inoculum.
[f] *C. resinae* inoculum.
[g] Sample used for chemical tests.
[h] First CH_2Cl_2 extract washed with water.

irradiation on the QUV tester was required to cause the same degradation. In this case successive extractions with methanol and dichloromethane were employed to obtain fractions of decreasing polarity. The high polymer fraction which was insoluble in both solvents supported minimal growth upon being microbially challenged. The oligomer fractions obtained by extraction with methanol and with dichloromethane exhibited similar pattern of microbial growth. Each successive fraction gave less profuse growth. This pattern was observed with ASTM media and BH agar.

With each polymer the same picture emerges: minimal growth was obtained with the insoluble high polymer fraction. The oligomer obtained from first extract produces maximum growth, but each succeeding extract gave oligomers supporting less growth. In most cases this pattern of growth

TABLE IV
Microbial Growth on Fractions Extracted from PE

Exposure[a] (h)	Solubility[b]	Solvent[c]	Microbial growth[d] ASTM[e]	Microbial growth[d] BH agar[f]
150	i	THF	0	0
150	—[g]	—[g]	+	+
150	s	1st THF	+++	++++
150	s	2nd THF	++	+++
150	s	3rd THF	+	++
0	—[h]	—	0	0

[a] Mercury arc.
[b] i = insoluble, s = soluble.
[c] First THF = first extracts with THF, etc.
[d] Growth after 70 days (+ slight, ++ moderate, +++ good, ++++ heavy growth).
[e] ASTM fungal spore mixture inoculum.
[f] *C. resinae* inoculum.
[g] Exposed, not extracted.
[h] Unexposed, not extracted.

TABLE V
Microbial Growth on Fractions Extracted from PP

Exposure[a]	Solubility[b]	Solvent[c]	Microbial growth[d]	
			ASTM[e]	BH agar[f]
75	i	$MeOH/CH_2Cl_2$	+	0
75	s	1st MeOH	++++	++++
75	s	2nd MeOH	+++	+++
75	s	3rd MeOH	+	++
75	s	1st CH_2Cl_2	++	++
75	s	2nd CH_2Cl_2	+	+

[a] Fluorescent lamps.
[b] i = insoluble, s = soluble.
[c] First MeOH = first extract with methanol, etc.
[d] Growth after 70 days (+ slight, ++ moderate, +++ good, ++++ heavy growth).
[e] ASTM fungal spore mixture inoculum.
[f] *C. resinae* inoculum.

is exhibited by both of the ASTM mixed fungal spore inoculum and *C. resinae.*

SUMMARY

Exposure of polyolefins to UV radiation results in the formation of distinct fractions having different physicochemical properties and different responses to microbial challenge. A volatile fraction is formed which is measured by the loss in weight of the sample. This apparently is rapidly dissipated into the biosphere.

An oligomeric fraction which is soluble in various solvents at room temperature or slightly elevated temperatures is also formed. A small amount of the oligomer is present in the polymers prior to irradiation. Irradiation of SPE results in formation of additional quantities of oligomer, but its concentration does not increase beyond a limiting value.

In the case of SPE, the high polymer undergoes a rapid decrease in average molecular weight (M_N) resulting from the photolytic cleavage of the polymer backbone. In addition to oligomer, this cleavage is accompanied by formation of a crosslinked fraction. This fraction is characterized by its insolubility in TCB at 150°C. The linear high polymer is soluble under these conditions.

We have attempted to illustrate the relationship between these fractions by assuming an initial photolytic cleavage of the polymer chain resulting in the simultaneous formation of the crosslinked fraction and augmentation of any preexisting oligomer fraction.

Cleavage of the main polymer chains and accumulation of crosslinked components results in accelerated embrittlement of SPE and a resultant loss of mechanical strength. The film abrades rapidly and ultimately may assume the form of a fine powder under the impact of environmental stress. It has been claimed that this type of reduction of particle size on a supramolecular level will render the polymer vulnerable to a progressive or sustained microbial attack. Potts[17] found that low molecular weight linear polyethylene species did support microbial growth if the MW did not exceed about 550. In some cases growth was observed on high polymers, provided

the MW distribution was such as to provide sufficient concentration of the low MW species to support growth.

Other workers have reported that polyethylenes are capable of supporting growth.[21,22] However, it is very difficult to measure the extremely slow rates of biodegradation observed in these experiments. A possible solution to this problem was demonstrated by Albertsson and Ranby.[23] These workers were able to demonstrate as little as 0.001% degradation using C_{14}-labelled polymers, but extremely low decomposition rates were found.

The biodegradation of PP has not been as fully investigated as polyethylene, but the information that is available indicates that it is very similar in this respect. The same authors who adduced evidence for the microbial susceptibility of PE obtained evidence for degradation of PP,[21,22] but Potts et al.[17] found that the amount of fungus growth supported by PP is very small.

The present work has demonstrated that common types of polyolefins contain small amounts of oligomer which give minimal evidence of microbial growth *in situ* when the intact polymer is challenged. However, if the oligomer is separated and challenged as a separate fraction, it supports growth. Initial oligomer concentration is dependent on manufacturing and processing conditions. UV irradiation of the polymer will increase the amount of the oligomer fraction, but probably not in excess of a limiting value determined by kinetic factors involved in oligomer formation and degradation. Microbial growth may also be affected by other polymer parameters such as the presence of crystallinity and crosslinking. Detection of growth is influenced by the sensitivity of the method used, which may be radiometric, manometric, visual, or microscopic. It is not surprising, therefore, that there can be conflicting reports in regard to the susceptibility of polyolefins to microbial challenge depending on the judgement criteria selected by the various investigators. The critical point is the significance of the growth with respect to degradation of the polymer. Growth per se is not sufficient to claim biodegradability of substrate in this instance.

Mechanical abrasion of light sensitive polyolefins that have been embrittled by exposure to UV radiation produces a fine polymer powder. In this form the polymer has a greatly increased surface area, and can come into intimate contact with soil and water microorganisms and their extracellular enzymes. It has been claimed that the finely divided polymers undergo enhanced and progressive microbiological attack.[24,13]

The present results suggest that it is the oligomer fraction of the photolyzed olefines that is susceptible to challenge by microorganisms. The appearance of enhanced growth in the finely divided polymer may be due to more rapid diffusion of the oligomer to particle surfaces. There is no evidence that the high polymer itself will undergo progressive attack by microorganisms as a result of any mechanical dispersion on a supramolecular level.

On the basis of the suggested modes for polymer photolysis, the primary nonvolatile products are crosslinked polymer and oligomer. Continued irradiation would result in further production of the crosslinked fraction. In fact, lengthy irradiation of SPE resulted in polymer residues which comprised almost 30% of the crosslinked fraction. This residue did not support

microbial growth, and it is expected that highly crosslinked polyolefins would be relatively recalcitrant to degradation by environmental agents, physical or biological.

Initiation of the photooxidation process involves the interaction of a number of factors including the light absorbing properties of the substrate, the emission spectrum of the source, and the energy transfer relationships on a molecular level in the substrate, including the effect of UV sensitizers. These considerations determine whether a sufficient concentration of energy will accumulate in a particular chemical bond to bring about its cleavage. Continuation of the photooxidation involves reaction of molecular oxygen with radicals formed by photolysis. In the case of polyolefins, this results in radical chain reactions which may terminate by crosslinking, branching, or reaction with impurities.

In the case of polyolefins which contain no impurities, light absorption does not occur at wavelengths above 200 nm. The presence of unsaturated impurities introduced by the thermal processing of commercial polyolefins permits absorption of light energy in the near UV region (200–400 nm). This may result in transfer of the light energy to the polyolefin itself resulting in initiation of the chemical breakdown of the polymer by cleavage of the carbon–hydrogen or carbon–carbon bonds.

The bond energy of the carbon–carbon bond is 83 kcal/mol while that of the carbon–hydrogen band is 99 kcal/mol. The energy of a photon is given by the expression

$$E\,(\text{kcal/mol}) = \frac{2.86 \times 10^5}{X\,(\text{Å})}$$

Therefore, it would require light of wavelength 3450 Å or less to cleave the carbon–carbon bond.

The light sources used in the present study exhibit different energy distribution as a function of wavelength. Thus, the quartz mercury lamp is rich in high energy photons, the fluorescent lamp is intermediate while the Xenon arc and sunlight contain less of the energy rich photons. Hence the proportion of radiated energy lying below 3450 Å will vary from source to source as will the fraction received by the polymer which is effective in breaking the bonds in the polyolefins.

The exposure of PE films to light sources possessing different spectral distribution for different exposure times produced oligomer fractions whose infrared spectra were virtually identical. Experiments involving PP and SPE films gave similar results, indicating that each of the sources emits a spectral component possessing enough energy to cause cleavage of the carbon–carbon bonds making up the backbone of each of the polymers substrates exposed. The similarity of the oligomeric fractions suggests that there is a common degradation mode for the differing energy sources including outdoor weathering. The quartz mercury arc whose spectrum is richest in short-wave high-energy radiation is able to cleave the highly crosslinked residues only with difficulty. After prolonged radiation these residues become a major polymer component. Under average conditions of outdoor illumination, the lower quantum energy, the effect of shade, clouds, and intermittent sunshine are factors. Under these conditions the decom-

position would be expected to be even slower. It does not appear then that residues from the degradation of polyalkylenes would be completely eliminated from the biosphere even by prolonged exposure to environmental agents including microorganisms.

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