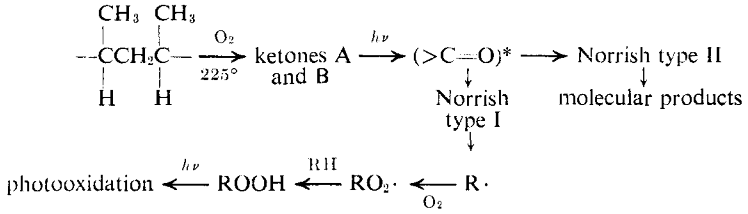
will probably exceed $RO_2\cdot$ formation, due to the high internal viscosity of the polymer, and the low dissolved O_2 concentration and O_2 permeability. Radical combination after reaction 1B is unlikely, however, since $CH_3\dot{C}O$ or $\dot{C}H_3$ can diffuse from the reaction site before recapture. Hydrogen abstraction by $CH_3\cdot$ or $CH_3\dot{C}O$ will then result in the formation of other (isolated) macroradicals. Hence, type I photolysis of polypropylene ketones is likely to be an important contributor to polypropylene photoinstability. The tentative mechanism can be summarized as



This mechanism is consistent with recent papers which show that many commercial uv stabilizers blended with polypropylene, such as some nickel chelates and several so-called light absorbers, probably act as energy acceptors from excited chromophores.[5,31] The triplet (and possibly some singlet) energy of the excited ketones can be transferred by resonance excitation to the stabilizer, where it is harmlessly dissipated, and type I dissociation prevented.

In conclusion, it appears that ketonic oxidation products introduced into polypropylene during processing do contribute to the photoinstability of the polymer. However, this does not exclude the possibility that other trace impurities such as aldehydes, α,β-diketones, conjugated unsaturation, peroxides or transition metals, or O_2–polypropylene charge-transfer complexes also play important roles.

Acknowledgments. The authors are grateful for gifts of polypropylene from Chemcell Ltd. Celanese Fibers Division, from Eastman Chemical Inter-American Ltd., and from Hercules Inc. Fibers and Film Department. Thanks are due Mr. J. D. Cooney for technical assistance.

(31) J. C. W. Chien and W. P. Conner, *J. Amer. Chem. Soc.*, **90**, 1001 (1968).

The Photodegradation of Polypropylene Films.
III. Photolysis of Polypropylene Hydroperoxides[1]

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ABSTRACT: Hydrogen-bonded hydroperoxide groups are believed to be the chief primary product in the photooxidation of polypropylene films in the near ultraviolet. The kinetics and mechanism of the photolysis of these hydroperoxides have been studied at 3650 Å in the solid state under high vacuum. A combination of infrared, glpc and chemical analysis showed that the primary photolytic step involved hydroperoxide cleavage into *t*-alkoxy and ·OH radicals. The major volatile photolysis product was water, which resulted from hydrogen abstraction by ·OH radicals. Little evidence was found for radical-induced hydroperoxide decomposition. The main polymeric products which were produced by reaction or decomposition of the alkoxy radicals have been tentatively identified. The *t*-alkoxy radicals are believed to undergo extensive β scission by two competing processes both of which produce ketonic products. One of these processes leads to scission of the polymer backbone, and is probably responsible for the large drop in intrinsic viscosity which resulted from hydroperoxide photolysis. The kinetics of hydroperoxide photolysis were followed by infrared analysis and by the continuous measurement of weight loss from each film sample during irradiation. An experimental overall quantum yield of about 4 was found for hydroperoxide photolysis, although the true value probably lies closer to unity. Hydroperoxide photolysis by sunlight in the presence of air is believed to represent a major source of free radicals and backbone scission during the photodegradation of polypropylene. This photolysis is probably prevalent both in the very early stages of and in the advanced stages of photodeterioration of commercial polypropylene articles.

Martin and Norrish have shown that the photolytic decomposition of *t*-butyl hydroperoxide in an inert solvent at 3130 Å occurs with a very high quantum yield (greater than unity).[2] This was attributed to a radical chain decomposition following an initial O–O

$$RO\text{—}OH \xrightarrow{h\nu} RO\cdot + \cdot OH \qquad (1)$$

scission. In solution, alkoxy radicals (RO·) are known to abstract hydrogen from many substrates, to combine with available free radicals, and to undergo β scission to give a ketone and an alkyl radical.[3,4]

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(1) N.R.C.C. No. 11010.

(2) J. T. Martin and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A220**, 322 (1953).

Polymeric hydroperoxides are believed to be major products in both the photooxidation,[5] and in the low-temperature thermal oxidation[6] of unstabilized polypropylene. Although the thermal decomposition of polypropylene hydroperoxide has been frequently studied,[7] little work has been published on its photolysis. However, by analogy with the solution photolysis of *t*-butyl hydroperoxide, photolysis of polymeric hydroperoxides can be expected to play an important part in the deterioration of polypropylene articles under weathering conditions, *i.e.*, exposure to terrestrial sunlight (>2900 Å) in air. In particular, hydroperoxide photolysis may lead to competing cross-linking and backbone scission reactions, together with the initiation of degenerate branching oxidation chains in the presence of oxygen.

In this paper we report an investigation of the photolysis of polypropylene hydroperoxides under high vacuum which was carried out in order to evaluate the extent of competing radical reactions in the solid polymer. Oxygen was excluded in order to reduce the expected complexity of the photolysis.

Experimental Section

Materials. The two types of predominantly isotactic polypropylene resin used comprised an unstabilized commercial resin (Hercules Profax 6801), and a stabilized extruded film (20 ± 2 μ, Eastman). The Hercules resin was in powder form, and was molded into (predominantly) smectic films of varying controlled thicknesses by the previously described procedures.[8] The extruded film was acetone extracted in a Soxhlet apparatus for 48 hr to remove uv and thermal stabilizers, followed by vacuum drying.

Film Oxidation. Oxidized polypropylene films were conveniently prepared by irradiation in air under a Hanovia lamp filtered through a Corning C.S. 7-54 plus a Corning C.S. 0-52 filter (transmission maximum 3750 Å). Irradiation temperature was ~35°. Hydroperoxide-containing films were also prepared from Profax 6801 resin which had been air oxidized at 225°.[8] The thermally oxidized resin was molded into films, and then photooxidized with the filtered Hanovia lamp to give film samples which contained controlled concentrations of both hydroperoxide and carbonyl substituents.

Film Characterization. Intrinsic viscosities were determined by dilution viscosity measurements in decalin at 135°. Viscosity molecular weights of the unoxidized polymer were calculated from the expression of Westerman.[9]

Infrared (ir) spectra were recorded on a Beckman IR8 spectrometer coupled to a scale expansion unit and 10-in. slave recorder. Spectra reproduced in this paper (Figures 4 and 5) were obtained at a times five scale expansion and a scan speed of ~90 $\mathrm{cm^{-1}\ min^{-1}}$ on the spectrometer; automatic slit control was used throughout. Spectral resolution was better than 3 $\mathrm{cm^{-1}}$. Noise level was less than 1.0% at 95% transmission, and was completely random across the 1900–1600-$\mathrm{cm^{-1}}$ range. Spectra were rescanned several times in order to ensure that the observed peaks and shoulders corresponding to the main hydroperoxide photolysis products (1760–1700-$\mathrm{cm^{-1}}$ region) were reproducible, and were not caused by random noise. The peaks and shoulders corresponding to these products were assigned by comparison with the reported ir spectra[8] of pure compounds dissolved in isooctane or 2,4-dimethylpentane. These model compounds were chosen so as to be of similar structure to the expected polypropylene derivatives. In addition chemical treatment of oxidized film samples with SF_4 was used to confirm the location of the $-C(=O)OH$ absorption at 1710 $\mathrm{cm^{-1}}$, and oxidation with HIO_4 was used to show the absence of dione products. Oxidized films also reacted readily with alkaline hydroxylamine and anhydrous methanolic hydrochloric acid indicating the presence of appreciable ketone or aldehyde. Mild oxidizing agents, however, failed to indicate any aldehyde. These chemical procedures have been described previously.[8] The 1726-$\mathrm{cm^{-1}}$ absorption was assumed to be caused by peresters,[10] and to have the same extinction coefficient as esters.

Complex ir envelopes caused by overlapping absorptions in the carbonyl region were resolved into their component peaks on a Du Pont 310 curve resolver. The component absorption bands, as produced by the IR8, have been shown[8] to be represented by skewed Lorentzian peaks with half-band widths of 14 $\mathrm{cm^{-1}}$. Although the best possible base line (curve a, Figure 5) was synthesized by the use of the base line inflection point controls on the curve resolver, five extra curves of fixed height were also required to produce a good approximation to the experimental base line. These curves are shown as broken lines in Figure 5. The seven other component peaks shown changed in height with extent of hydroperoxide photolysis. The peak at 1735 $\mathrm{cm^{-1}}$ does not correspond to a resolved peak or shoulder in any of the recorded spectra, but its inclusion was found to improve the agreement between the experimental and synthetic envelopes. The measured height of this peak is consequently of very limited significance (up to 50% error possible). Repeated attempts at resolution of a given spectrum, using *curves at the indicated frequencies in Figure 5*, reproduced peak heights to within 10% for the 1700-, 1710-, 1718-, and 1726-$\mathrm{cm^{-1}}$ components and to within 20% for the 1745- and 1762-$\mathrm{cm^{-1}}$ components. To establish further the reliability of the resolution technique, the ir spectra of isooctane solutions containing methyl *n*-butyrate, 2-ethylhexanal, 2,4,8-trimethyl-4-nonanone, and octanoic acid at various concentrations (1 × 10^{-2} *M* or greater) were recorded. All four components were detected as discrete peaks or shoulders by the spectrometer. The spectra were then resolved into component peaks on the Du Pont curve resolver. The height of each synthesized component was then compared with the height of the ir band given by this component when dissolved alone at the same concentration as in the mixture. Agreement between these latter heights, and the peak heights determined by resolution of the mixture spectra, was again usually better than 10%. The authors are grateful for the suggestion by the referees of this test of the resolution technique.

All photooxidized film samples showed a broad featureless absorption centered at ~3400 $\mathrm{cm^{-1}}$, which was attributed to hydrogen-bonded –OH groups (both alcohol and hydroperoxide). Hydrogen-bonded alcohol and hydroperoxide derivatives of polypropylene were assumed to have the same extinction coefficients (based on peak heights) as *t*-butyl alcohol and *t*-butyl hydroperoxide, respectively.

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(3) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **89**, 4891 (1967).

(4) J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, **30**, 3272 (1965).

(5) Y. Kato, D. J. Carlsson, and D. M. Wiles, *J. Appl. Polym. Sci.*, in press.

(6) J. C. W. Chien, E. J. Vandenberg, and H. Jabloner, *J. Polym. Sci.*, **6**, 381 (1968).

(7) (a) L. A. Tatarenko and V. B. Pudov, *Vysokomol. Soedin.*, **B10**, 287 (1968); (b) J. C. W. Chien and H. Jabloner, *J. Polym. Sci. Part, A-1*, **6**, 393 (1968).

(8) D. J. Carlsson and D. M. Wiles, *Macromolecules*, **2**, 587 (1969).

(9) L. Westerman, *J. Polym. Sci., Part A-1*, **1**, 411 (1963).

(10) J. P. Luongo, *J. Polym. Sci.*, **42**, 139 (1960).

Solutions of these compounds in isooctane at four concentrations gave hydrogen-bonded –OH peaks at 3400 cm^{-1}. The apparent extinction coefficients for hydrogen-bonded –OH were extrapolated to infinite concentration. This gave limiting values for bonded –OH extinctions of 70 ± 7 M^{-1} cm^{-1} (*t*-butyl hydroperoxide) and 150 ± 15 M^{-1} cm^{-1} (*t*-butyl alcohol). Free –OH peaks (reported at 3553 cm^{-1} in polypropylene hydroperoxide[6]) were not detected in any of the oxidized polypropylene films.

The attempted preparation of large areas (6 cm × 15 cm) of uniformly photooxidized film by the irradiation of the Eastman extruded film was only partially successful. The ir transmission spectra of such an oxidized film showed quite wide, erratic variations in hydroperoxide concentration which were not caused by any obvious feature of the irradiation conditions. Consequently, great care had to be taken in the selection of film areas on which several comparative destructive analyses were to be performed. Identical –OH absorption at 3400 cm^{-1} was taken as the criterion of similar degrees of oxidation. Total areas of ~18 cm^2, of 20-μ film, were usually required for the study of initial and final peroxide content and molecular weight, and for the determination of weight loss during irradiation.

Peroxide Determinations. The peroxide concentrations of oxidized film samples were determined by a combination of the methods of Mair and Graupner[11] and Uri.[12] Film fragments (5–10 mg) were refluxed with 2.0 ml of a sodium iodide solution in isopropyl alcohol (200 g $l.^{-1}$) after acidification with 7 ml of an acetic acid/isopropyl alcohol mixture (1:10 ratio by volume). At the end of the reflux period, the solution was cooled, diluted to 10 ml with distilled water, and the I_3^- formed during the peroxide decomposition was determined on a Cary 15 uv spectrometer. Optical densities were determined at 3600 Å in 1- or 0.1-cm quartz cells and peroxide concentrations were estimated from a measured extinction coefficient for I_3^- of 25000 M^{-1} cm^{-1}. Reagent blanks were estimated on duplicate refluxes. With the above procedure, it is possible to take advantage of the oxidative stability of iodide ions in isopropyl alcohol solutions (obviating the need for nitrogen blanketing), and the high sensitivity and convenience of a spectrophotometric method. Only a brief reflux (~5 min) is normally required to give a quantitative yield of I_3^- from most hydroperoxides.[11] However, the production of I_3^- from a film sample is limited by the slow diffusion of reagents into the polymer. A reflux period of 30 min was found necessary to give complete decomposition of peroxides in films of up to 40 μ in thickness. Complete decomposition was confirmed by the failure of the film sample to generate further I_3^- during a short reflux in fresh reagents. Because of the prolonged reflux conditions required, the method gives a peroxide value which represents the sum of the concentrations of hydroperoxides, and several types of peroxides in each film sample.[11] When 1-cm absorption cells are used, this procedure allows the estimation of total peroxide levels as low as 1×10^{-7} mol in a film fragment of about 5 mg weight.

Hydroperoxide determination by the SO_2 method recommended for polyethylene hydroperoxides[13] was unsuccessful. Film evacuation followed by treatment with gaseous SO_2 resulted in the loss of most of the –OH absorption at 3400 cm^{-1}, but the predicted ir bands at 1195 cm^{-1} were not detected. This effect might possibly be caused by the high degree of hydrogen bonding in peroxidized polypropylene. Alcohol (ROH) concentrations were, however, determined from the residual 3400-cm^{-1} absorption after film treatment with SO_2. SF_4 treatment of oxidized film samples caused the complete loss of all –OH ir absorptions, and in addition allowed an independent estimation of carboxylic acids in the sample.[14] Comparison of ir spectra taken before and after SF_4 treatment allowed accurate estimation of the total –OH optical density (O.D.) at 3400 cm^{-1}. When SF_4 treatment was impractical, $O.D._{3400}$ was estimated from a comparison with the ir spectrum of an unoxidized film sample of similar thickness. Carboxylic acid–OH absorption occurs at ~3180 cm^{-1}, and so does not interfere with alcohol/hydroperoxide estimations by ir spectroscopy. Since SF_4 is not expected to attack peroxides (ROOR), peroxide concentration in the presence of hydroperoxides was estimated by the I_3^- method outlined above, after film treatment with SF_4. By combining the above analytical techniques, ROOR, ROH, and ROOH concentrations can be separately determined, although di-*t*-alkyl peroxides may not produce I_3^- during the total peroxide determination.[11] Experimental values for the three concentrations are not expected to be better than ±20%, because of uncertainties in the ir extinction coefficients, and the weak –OH absorptions normally found.

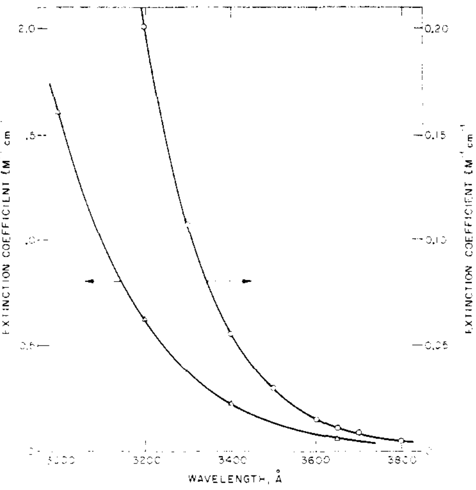

Figure 1. Uv absorptions of model compounds: Δ, di-*t*-butyl peroxide; ⊙, *t*-butyl hydroperoxide.

Uv Absorptions. Direct experimental determination of the uv extinction coefficients (3000–3800 Å) for polypropylene hydroperoxide in oxidized film was attempted. Scatter due to reflection from the film faces was eliminated by the immersion of the films in a solvent of identical optical density,[15] such as *cis*-decalin. Immersion of ten unoxidized 20-μ polypropylene films in *cis*-decalin gave very low optical density from 4000 to 2500 Å. Similar measurements on ten 20-μ hydroperoxide-containing films (0.35 *M*) gave virtually zero O.D. (<0.002) down to ~3400 Å, followed by a steady, approximately exponential increase in O.D. This increase was attributed to the presence of several types of oxidation product, including unsaturation. After complete destruction of the hydroperoxide, these same film samples showed zero O.D. down to 3600 Å, followed by a more rapid exponential rise in O.D. This effect was probably caused by the generation of some unsaturated products during hydroperoxide decomposition, and masks any absorption changes due to hydroperoxide loss. Experimental determination of the extinction coefficients on bulk polypropylene hydroperoxide (even atactic polymer) is probably also impractical due to the low value expected, and the difficulty of obtaining high concentrations of pure hydroperoxide dis-

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[11] R. D. Mair and A. J. Graupner, *Anal. Chem.*, **36**, 194 (1964).

[12] F. W. Heaton and N. Uri, *J. Sci. Food Agr.*, 781 (1958).

[13] J. Mitchell and L. R. Perkins, *Applied Polym. Symp.*, **4**, 167 (1967).

[14] J. F. Heacock, *J. Appl. Polym. Sci.*, **7**, 2119 (1963).

[15] R. H. Partridge, *J. Chem. Phys.* **45**, 1679 (1966).

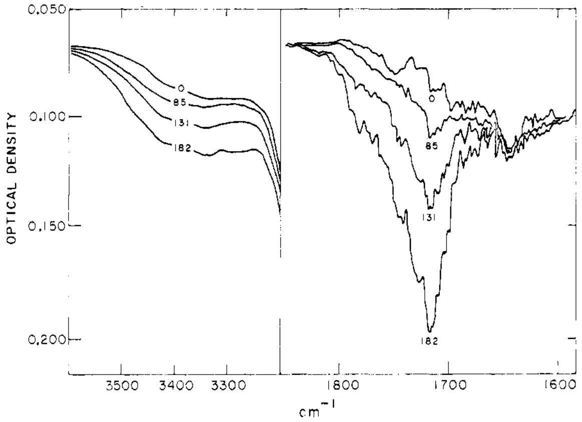


Figure 2. Ir changes during photooxidation at 3650 Å. Film, 80-μ thickness, irradiation in air with Hanovia lamp at 35°. Captions on each curve refer to total irradiation time in hours.

solved in a nonabsorbing solvent. Consequently, the uv absorption curves for purified *t*-butyl hydroperoxides and di-*t*-butyl peroxide in a region important to the weathering of polymers (3000–3800 Å) were determined in isooctane solution or in bulk (Figure 1). These curves were assumed to approximate to the absorptions of the corresponding polypropylene derivatives. The molar extinction coefficients plotted in Figure 1 were used in quantum yield calculations.

Film Degradation. Oxidized film samples were degraded under vacuum by irradiation with the filtered beam from an Osram mercury lamp (SP 500W). The beam was filtered through Corning filters CS 7-54 plus CS 0-52 (transmission maximum 3750 Å, half-band width 350 Å). With these filters and light source, the maximum energy absorption by hydroperoxides occurs at 3650 Å, and this value is taken as the wavelength of photolysis. The degradation was followed by the change in sample weight as measured by a Cahn electrobalance and by ir analysis. Volatile degradation products were collected and analyzed by gas–liquid partition chromatography (glpc). The optical system and all experimental procedures have been described previously.[8]

Results

Controlled air oxidation of unstabilized isotactic polypropylene, either thermally (at ~80°) or photochemically at relatively long wavelength (~3700 Å), causes a gradual buildup of polypropylene hydroperoxides. An example of this change is shown by the ir absorptions at 3400 cm^{-1} in Figure 2. Despite these relatively mild conditions, accumulation of carbonyl products (1800–1650 cm^{-1}) always accompanies the hydroperoxide buildup (Figure 2). Consequently, vacuum photolysis of the hydroperoxides in these films is also likely to be accompanied by photolysis of some of the carbonyl products. However, the uv photolysis of polypropylene ketones has been studied at several wavelengths,[8] and since ketonic products will be shown to constitute the bulk of the carbonyl absorption, this photolysis can easily be separated from the much more rapid hydroperoxide photolysis at the relatively long photolysis wavelength.

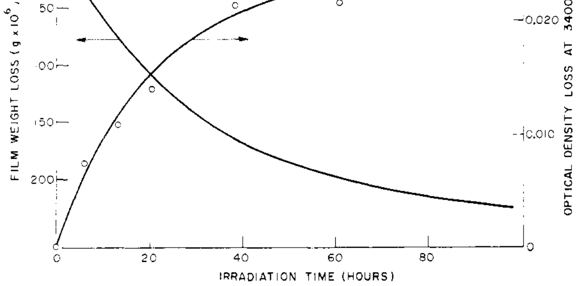


Figure 3. Weight and –OH absorption changes during irradiation. Film I, irradiation at 3650 Å, $\Sigma\epsilon_\lambda I_\lambda = 1.0 \times 10^{-4}$ kcal sec^{-1}; film 22-μ, 0.0281 g. Continuous evacuation at 10^{-5} mm.

Table I
Photolysis Products from Polypropylene Hydroperoxides[a]

Compound	Yield, mol × 10^6
H_2O	~1.4
CO_2	~0.1
CH_4	0.06
CO	0.03[b]
CH_3COCH_3	0.035[c]
CH_3COOH	~0.02
$HOCH_2COCH_3$	~0.03
CH_3OH	0.007
CH_3CHO	0.010[c]
$CH_3COCH_2CH_3$	0.010
C_3H_6	0.010
C_2H_4	0.004
C_2H_6	0.004
C_4H_8	0.003
$CH_3CH(CH_3)OH$	~0.002
O_2	<0.1
H_2	N.D.

[a] Film sample, 37 μ thickness, 0.0192 g, irradiated at 3650 Å for 73 hr, intensity 1.0 × 10^{-4} kcal sec^{-1} on sample, cell temperature 30°. ROOH loss during irradiation = 1.7 × 10^{-6} mol. [b] Products resulting from ketone A photolysis. [c] Products resulting from ketone B photolysis.

Uv irradiation of a hydroperoxidized film on the Cahn electrobalance results in a rapid initial weight loss, followed by a gradual decrease to an approximately constant weight. This weight loss is accompanied by a corresponding decrease in the ir absorption at 3400 cm^{-1}. These time dependent changes are shown in Figure 3. SF_4 treatment and total peroxide determination on the film after irradation to constant –OH absorption indicated the presence of virtually no residual polypropylene hydroperoxide, some alcohol, and some peroxide. The decrease in hydroperoxide concentration during irradiation is accompanied by the evolution of volatiles and the formation of polymeric carbonyl products. The changes in carbonyl ir absorptions are shown in Figure 4. The composition of the major volatiles (individually >0.1 mol % of the total product) collected during complete hydroperoxide photolysis is shown in Table I. Quantitative determinations of polar products (H_2O, CH_3COOH, $HOCH_2COCH_3$) are expected to be accurate to no better than ±30% due to adsorption problems during transfer to the glpc. The glpc analysis shows that the main photolytic process is hydroperoxide decomposition to give an approxi-

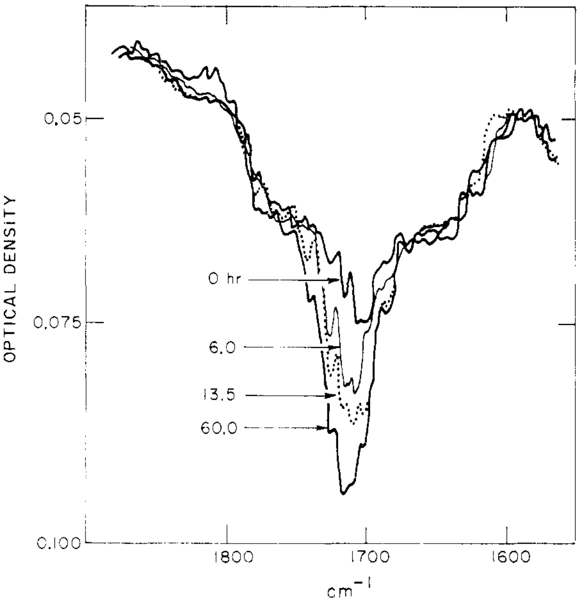


Figure 4. Changes in carbonyl ir absorption during hydroperoxide photolysis. Experimental details and film sample as for Figure 3. Captions on each curve refer to total irradiation time in hours.

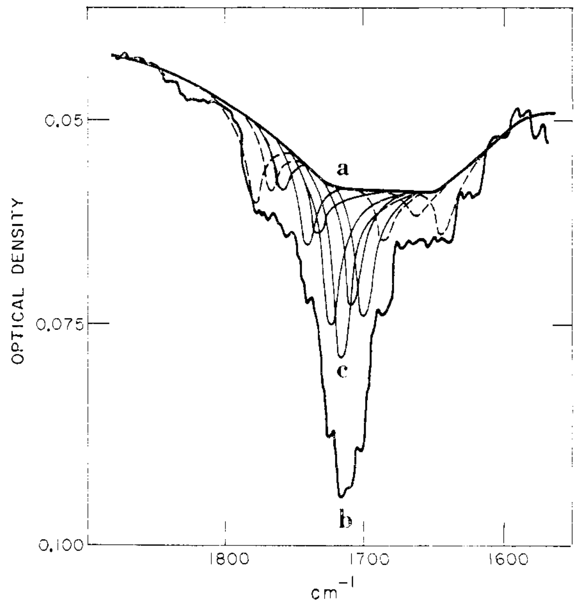


Figure 5. Resolution of complex carbonyl ir absorption: A, Du Pont curve resolver base line; B, experimental envelope (60 hr curve, Figure 4); C, component ir absorptions. Broken lines represent peaks required to simulate the experimental base line.

mately quantitative yield of water together with some products resulting from the slow photolysis of the carbonyl derivatives [*cf.* Table III, ref 8]. These products are indicated in Table I. A quantitative estimation of oxygen evolution during irradiation was not possible due to the slight oxygen blank which was always detected during irradiation, presumably caused by desorption from the cell and sample. A hydroperoxide determination on the condensable volatile products showed the complete absence of H_2O_2. Irradiation of an unoxidized, but otherwise identical film sample gave only a trace of hydrogen as the volatile product. Irradiation of oxidized film samples of varying thickness and varying initial hydroperoxide concentration resulted in no obvious changes in the composition of the volatile products. Although water is formed during hydroperoxide photolysis, the –OH absorption detected in most film samples at 3400 cm^{-1} was not caused by adsorbed water. This was demonstrated by the immersion of an oxidized film sample in water. A strong –OH absorption due to adsorbed water was produced, but was completely lost after only a few minutes' evacuation, whereas the –OH absorption normally associated with oxidized film samples is unaffected by evacuation.

The complex carbonyl ir absorption envelopes obtained during hydroperoxide photolysis (Figure 4) were reduced to their component peaks on the Du Pont curve resolver. An example of this resolution is indicated in Figure 5. The locations of six of the seven component peaks shown as solid lines (Figure 5) were determined from a study of the reproducible peaks and shoulders observed in the spectra of the film sample at varying degradation times. (As mentioned previously the minor 1735-cm^{-1} component was never resolved.) The seven peaks were tentatively assigned from a comparison with the ir spectra of pure compounds, in solvents structurally related to polypropylene.[5] In addition, the assignments of the 1718- and 1726-cm^{-1} peaks were inferred by a comparison with the relatively simple high-temperature carbonyl oxidation products of polypropylene.[8] This work showed that the peaks at 1762 ($-C(=O)OOC<$), 1745 ($-C(=O)OC<$), 1735 ($-C(=O)H$), 1726 ($-CH(CH_3)CH_2C(=O)CH_3$), 1718 ($-CH(CH_3)CH_2C(=O)CH_2CH(CH_3)$), 1710 ($-C(=O)OH$), and 1700 cm^{-1} ($>C=CC(=O)OH$) all increased in intensity during photolysis. Several other peaks are shown as broken lines in Figure 5. These peaks were required to reproduce the complete experimental envelope; during irradiation, however, no change was detected in them. In particular, no significant change was noticed in the ethylenic unsaturation at ~1645 cm^{-1}. Changes in concentration of the polypropylene carbonyl derivatives with irradiation time were calculated from reported extinction coefficients[8] and peak heights derived from the resolved ir curves. These concentration changes are shown in Figure 6. Various sources of error such as the assumed frequency and half-band width

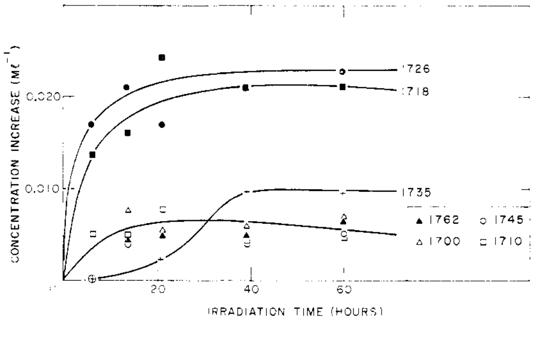
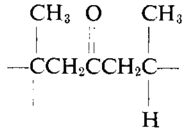
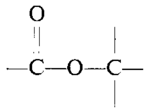
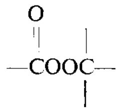
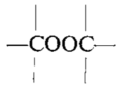
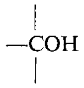
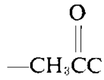
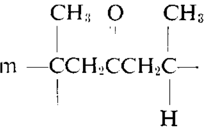


Figure 6. Carbonyl product formation during hydroperoxide photolysis; experimental details as in Figure 3. Captions on curves refer to ir absorption maxima (cm^{-1}).

TABLE II

COMPLETE PHOTOLYSIS PRODUCTS FROM POLYPROPYLENE HYDROPEROXIDES[a]

	Product yield, mol, film I	Average major product yield, mol %, ROOH loss	
Polymeric products			
$-CH_2C(=O)CH_3$	0.021	~50-70	50[b]
 $-\overset{\overset{CH_3}{\mid}}{\underset{\mid}{C}}CH_2\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{CH_3}{\mid}}{\underset{\underset{H}{\mid}}{C}}-$	0.023		
Total -COOH	0.012		
-CHO	0.010		
 $-\overset{\overset{O}{\|}}{C}-O-\overset{\mid}{\underset{\mid}{C}}-$	0.005		
 $-\overset{\overset{O}{\|}}{C}OO\overset{\mid}{\underset{\mid}{C}}-$	0.005		
 $-\overset{\mid}{\underset{\mid}{C}}OO\overset{\mid}{\underset{\mid}{C}}-$	0.027	5-10	~30[b]
 $-\overset{\mid}{\underset{\mid}{C}}OH$	≤0.010	5-10	15-20[b]
Volatile products			
From  $-CH_3\overset{\overset{O}{\|}}{C}CH_3$ photolysis	~0.001		
From  $-\overset{\overset{CH_3}{\mid}}{\underset{\mid}{C}}CH_2\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{CH_3}{\mid}}{\underset{\underset{H}{\mid}}{C}}-$ photolysis	~0.001		
CH_3COOH	~0.002		
$HOCH_2COOCH_3$	~0.001		
H_2O	0.13		80-90[b]
Hydroperoxide loss	0.14		

[a] Irradiated at 3650 Å, intensity 1.0 × 10^{-4} kcal sec^{-1} on sample. Continuous evacuation at 10^{-5} mm, during irradiation unless otherwise stated. [b] Evacuated to 10^{-5} mm and then sealed prior to irradiation, or 5 mm of H_2 introduced prior to seal-off.

of the component peaks, uncertainty in ir extinction coefficients, and reproducibility of the Du Pont curve resolver technique probably lead to total error limits of within ±30% (for 1700, 1710, 1718 and 1726 cm^{-1}), ±50% (1745 and 1762 cm^{-1}), and close to ±100% (for the unresolved 1735 cm^{-1}) in the reported concentrations. The major decomposition products produced by the photolysis of polypropylene hydroperoxide, in a specific film sample, are collected in Table II. This list is based on the ir changes and chemical analyses of each film, before and after irradiation, and the known distribution of volatile products. Alcohol formation during irradiation was very low, although an initial alcohol concentration (~0.023 *M*) was present in the film sample. Average results for the photolysis of many samples under similar conditions are collected in Table II. Also shown are results obtained during irradiation of films in the sealed cells which were frequently used to collect volatiles for glpc analysis. Introduction of 5 mm of hydrogen prior to the seal-off of these cells did not affect the analytical results.

Ultraviolet degradation of polypropylene hydroperoxide under vacuum was found to be accompanied by a pronounced drop in intrinsic viscosity [η]. For example, on photooxidation of an unstabilized Eastman film (20 μ) at 3750 Å to a hydroperoxide concentration of 0.34 *M*, [η] fell from 2.035 dl g^{-1} ($\overline{M}_v \sim 3.5 \times 10^5$)

to 0.571 dl g^{-1}. Subsequent complete hydroperoxide photolysis under continuous evacuation caused a further drop in $[\eta]$ to 0.409 dl g^{-1}, whereas photolysis under hydrogen caused $[\eta]$ to drop to 0.436 dl g^{-1}.

Quantum Yield. The quantum yield for hydroperoxide photolysis can be calculated from the weight– and O.D.–time curves shown in Figure 3. In all photolyses, the absorbed light intensity was less than 0.1% of the incident intensity. Under these conditions, first-order decomposition of hydroperoxide groups is governed by the expressions

$$-\mathrm{d}[\text{O.D.}^{3400}]_t/\mathrm{d}t = 2.303 l \Phi_\lambda \sum_{\lambda_1}^{\lambda_2} \epsilon_\lambda I_\lambda [\text{O.D.}^{3400}]_t \quad (2)$$

$$-\mathrm{d}(\mu\mathrm{g})/\mathrm{d}t = \frac{2.303 \times 10^6}{70} \Phi_\lambda \sum_{\lambda_1}^{\lambda_2} \epsilon_\lambda I_\lambda M [\text{O.D.}^{3400}]_t \quad (3)$$

Φ_λ is the over-all quantum yield for hydroperoxide photolysis between wavelength limits λ_1 and λ_2, $[\text{O.D.}^{3400}]_t$ the O.D. due to hydroperoxide, $\mathrm{d}[\text{O.D.}^{3400}]_t/\mathrm{d}t$ the rate of change of optical density, $\mathrm{d}(\mu\mathrm{g})/\mathrm{d}t$ the rate of weight change of the film sample (micrograms per second), all at time t, ϵ_λ the uv molar extinction coefficient, and I_λ incident light intensity (einsteins per second) on the sample at wavelength λ, l the film thickness, and M the weight loss (in grams) for photolysis of 1 mol of hydroperoxide. An M value of 18 g/mol has been assumed. The experimental weight loss per mol of hydroperoxide was found to be 22 ± 4 g. The summation

$$\sum_{\lambda_1}^{\lambda_2} \epsilon_\lambda I_\lambda$$

was calculated from the uv absorption curve for the hydroperoxide (Figure 1), the filter transmission data, and the known spectral energy distribution of the light source.[8] At the low rates of weight loss encountered during hydroperoxide photolysis, diffusion control of weight loss will not arise for samples of thickness less than 70–80 μ.[8] Since little alcohol –OH was formed during photolysis, the total change in $[\text{O.D.}^{3400}]$ will be equivalent to the loss of hydroperoxide only.

Quantum yields can also be determined from the integrated expressions

$$\ln\,[\text{O.D.}^{3400}]_t = \text{constant} - 2.303\Phi_\lambda \frac{lt}{v} \sum_{\lambda_1}^{\lambda_2} \epsilon_\lambda I_\lambda \quad (4)$$

$$\ln\,[\Delta(\mu\mathrm{g})_\infty - \Delta(\mu\mathrm{g})_t] = \text{constant} - 2.303\Phi_\lambda \frac{lt}{v} \sum_{\lambda_1}^{\lambda_2} \epsilon_\lambda I_\lambda \quad (5)$$

$\Delta(\mu\mathrm{g})_\infty$ is the total weight loss on complete hydroperoxide photolysis, $\Delta(\mu\mathrm{g})_t$ the weight loss at time t, and v the sample volume in liters. Both the weight– and O.D.–time data shown in Figure 3 fit the logarithmic expressions 4 and 5 quite well. Φ values were also calculated from the slopes of logarithmic plots for both types of data. All four methods were found to give similar values for Φ. Average over-all quantum yields calculated from the above four relationships are shown in Table III for several film samples. Even after complete hydroperoxide photolysis, a slow residual weight decrease was always recorded. This was mainly attributed to the photolysis of the weakly absorbing polymeric carbonyl products. A correction for this carbonyl photolysis was applied across each weight loss curve before the calculation of the quantum yields given in Table III. The correction is negligible in comparison with $-\mathrm{d}(\mu\mathrm{g})/\mathrm{d}t$ from the hydroperoxides at the start of degradation. The residual rates of weight loss due to carbonyl groups were in approximate agreement with the theoretical values, calculated from the quantum yields determined for the photolysis of polypropylene ketones.[8] Experimental scatter of the quantum yields quoted in Table III is about ±25%.

TABLE III

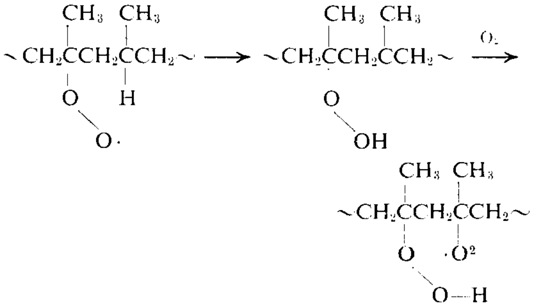
QUANTUM YIELDS FOR POLYPROPYLENE HYDROPEROXIDE PHOTOLYSIS AT 3650 Å

Film thick-ness, μ	Resin type	Initial hydro-peroxide concen-tration, M	Initial O.D. at 1721 cm^{-1}	Φ
39	Profax 6801	0.092	0.067	3.4
21	Eastman	0.27	0.061	4.8
22	Eastman	0.14	0.012	4.2

Within the narrow concentration range studied, hydroperoxide concentration was found to have no obvious effect on the over-all quantum yield (Table III). Similarly the presence of a high initial concentration of carbonyl products did not materially affect Φ. For each film sample, weight loss was found to be linearly dependent on residual hydroperoxide concentration down to zero concentration. The logarithmic relationships (eq 4 and 5) were also quite accurately obeyed down to complete hydroperoxide decomposition.

Discussion

During the photooxidation of polypropylene at ambient temperatures hydroperoxides may result from attack at the primary, secondary, or tertiary C–H bonds. Thermal oxidation of low molecular weight analogs of polypropylene, such as 2,4-dimethylpentane,[16] has been reported to involve a "back-biting" by the peroxy radicals to generate a sequence of neighboring 1,3-*t*-hydroperoxides. This



mechanism has also been reported to occur during

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(16) F. F. Rust, *J. Amer. Chem. Soc.*, 79, 4000 (1957).

thermal oxidation of polypropylene[6,17a] to give extensively hydrogen bonded hydroperoxides. However, this mechanism has been disputed by Tobolsky, *et al.*[17b] Chien has shown that isolated hydroperoxide groups in thermally oxidized polypropylene constitute less than 10% of the total hydroperoxide concentration, and that the bulk of the polypropylene hydroperoxide groups occur as dimer, trimer, or longer sequences.[6] Sequential attack (reaction 6) may also occur during the photooxidation of polypropylene in the solid phase, although the absence of free –OH in the ir spectrum of the oxidized polymer (Figure 2) may arise from interchain hydrogen bonding to oxidation products, as well as from intramolecular bonding.

Radiation of wavelength 3650 Å is sufficiently energetic (78 kcal einstein^{-1}) to cleave the RO–OH, and possibly also the $R{-}O_2H$ bond (42 and 70 ± 2 kcal mol^{-1}, respectively[18]). However, the $RO_2{-}H$ bond is unlikely to break (90 ± 2 kcal mol^{-1}).[18] Although the activation energy of photolytic scissions is only ~5% of the dissociation energy of the bond which is cleaved,[19] the large difference in bond dissociation energy between RO–OH and $R{-}O_2H$ will mean that reaction 1 can be expected to be the dominant primary photolysis step. Alkoxy radicals have been reported to exist during the uv irradiation of polypropylene hydroperoxide below 150°K,[20] although this work has not been confirmed.[21] Because of the large energy differences between the 3650 Å quantum and the RO–OH band dissociation energy, the normally highly reactive ·OH radicals produced in reaction 1 will be energetically hot, and will immediately abstract hydrogen from any convenient substrate to give water. Some hydroxyl radical dimerization to give H_2O_2 may possibly occur in third body collisions, although no H_2O_2 was detected in the photolysis products.

In the absence of rapid intersystem crossing from the first excited state, the method of Reinisch and Gloria[19] can be used to calculate approximate theoretical quantum yields for photolytic reactions in polymers. Based on an O–O bond strength of 42 kcal mol^{-1}, this method predicts a primary quantum yield of 0.7 for hydroperoxide photolysis by reaction 1. The higher over-all quantum yields determined experimentally (Table III) for the photolysis of polypropylene hydroperoxide may arise in several ways. Since the primary radicals (reaction 1) will probably be generated adjacent to one or more hydroperoxide groups,[6] a radical-induced decomposition of hydroperoxide similar to that detected in solution[2,22] is possible (reaction 7). Induced

$$\left.\begin{matrix}HO\cdot\\RO\cdot\end{matrix}\right\} + ROOH \longrightarrow \left.\begin{matrix}H_2O\\ROH\end{matrix}\right\} + RO_2\cdot \qquad (7)$$

hydroperoxide decomposition is, however, not indicated by the experimental results, since the water yield was roughly quantitative (Table I) and the weight loss per mole of hydroperoxide (~22 g/mol) indicates that each hydroperoxide group photolyzed to give an ·OH radical. The low alcohol yield, and independence of the over-all quantum yield on initial hydroperoxide concentration and on extent of photolysis also point to the absence of significant radical-induced decomposition. The photosensitized decomposition of *t*-butyl hydroperoxide by aromatic ketones has been found in solution.[23] Energy transfer to hydroperoxide groups from the alkyl carbonyl chromophores in oxidized polypropylene might, therefore, also contribute to a high experimental quantum yield. However, the Φ values shown in Table III show no dependence on the initial carbonyl content of the film samples. The most likely explanation of the apparently high experimental quantum yield probably lies in an underestimation of the uv extinction coefficient (ϵ_λ) of polypropylene hydroperoxide. Since the direct determination of actual ϵ_λ appeared to be experimentally impracticable, the adoption of the ϵ_λ values for *t*-butyl hydroperoxide (Figure 1) seemed reasonable. In view of the lack of information in the literature on the uv absorption spectra of hydroperoxides, and the difficulty of obtaining reasonable quantities of extremely pure hydroperoxides (*i.e.*, free from absorbing impurities, such as carbonyl compounds) other than the *t*-butyl, it is not possible to predict the effects of increasing size of the alkyl substituents on the extreme limits of the uv absorption. The reported absence of detectable *t*-butyl hydroperoxide photolysis at 3400 Å[2] does, however, point to a uv extinction for polypropylene hydroperoxide highter than that shown in Figure 1. In addition, the effects of phase, temperature, and polarity of the medium on the extreme tail of this type of uv absorption are not known. Consequently, the agreement between the experimental quantum yield of 4 and an expected quantum yield of about unity seems quite acceptable. This (relatively) good agreement also seems to support the absence of a sensitized hydroperoxide photolysis, although a contribution from traces of polymerization catalysts (specifically Ti compounds[24]) cannot be completely discounted.

Hydrogen abstraction from the polypropylene molecules by the primary radicals ·OH and RO· will produce alkyl radicals, which, in the presence of oxygen,

$$\left.\begin{matrix}HO\cdot\\RO\cdot\end{matrix}\right\} + RH \longrightarrow \left.\begin{matrix}H_2O\\ROH\end{matrix}\right\} + R\cdot \qquad (8)$$

will react to give peroxy radicals, and so propagate oxidation chains (reaction 6). The alkoxy radicals can also decompose by β-scission processes, which will play important roles in backbone scission, and alkyl radical formation. Photolysis of primary and secondary hydroperoxides will give primary and secondary alkoxy radicals, which can be expected to decompose by the β-scission steps[25]

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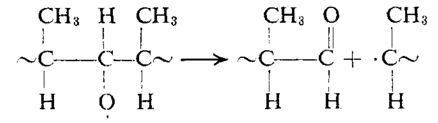
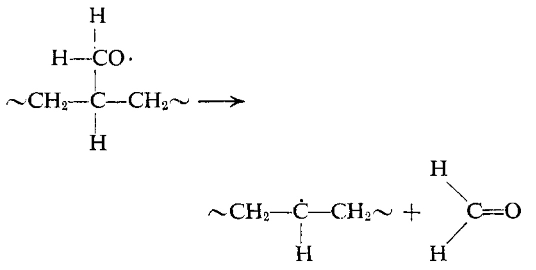


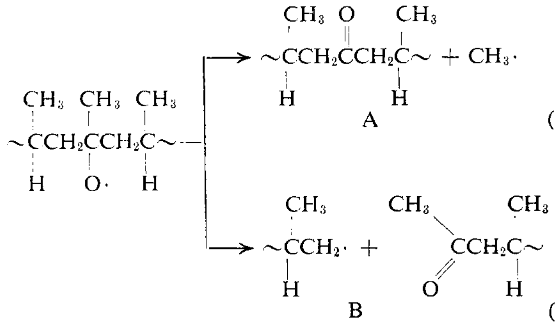
$$\sim\underset{H}{\overset{CH_3}{C}}-\underset{O\cdot}{\overset{H}{C}}-\underset{H}{\overset{CH_3}{C}}\sim\ \longrightarrow\ \sim\underset{H}{\overset{CH_3}{C}}-\underset{H}{\overset{O}{\overset{\|}{C}}}+\cdot\underset{H}{\overset{CH_3}{C}}\sim \qquad (9)$$



$$\sim CH_2-\underset{H}{\overset{H-\overset{H}{C}O\cdot}{C}}-CH_2\sim\ \longrightarrow\ \sim CH_2-\underset{H}{\dot{C}}-CH_2\sim+H_2C{=}O \qquad (10)$$

The relatively low yield of polymeric aldehyde products and the absence of formaldehyde observed during hydroperoxide photolysis support the conclusion that little primary or secondary C–H attack occurs during polypropylene photooxidation. The apparently anomalous aldehyde buildup (Figure 6) is probably due to gross experimental error in the estimation of very small aldehyde absorbances in the presence of large neighboring peaks (at 1726 and 1718 cm^{-1}).

After hydroperoxide photolysis, the carbonyl ir absorption of polypropylene is dominated by two major components, at 1726 and 1718 cm^{-1} (Figure 6). From a comparison with the ir absorption of model carbonyl compounds,[8] these peaks are attributable to polymeric ketones which may arise from β scission of the tertiary alkoxy radicals produced by *t*-hydroperoxide photolysis. The *t*-alkoxy radical can scission by two alternative pathways



$$\sim\underset{H}{\overset{CH_3}{C}}CH_2\underset{O\cdot}{\overset{CH_3}{C}}CH_2\underset{H}{\overset{CH_3}{C}}\sim\ \longrightarrow\ \underset{A}{\sim\underset{H}{\overset{CH_3}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_2\underset{H}{\overset{CH_3}{C}}\sim}+CH_3\cdot \qquad (11)$$

$$\longrightarrow\ \sim\underset{H}{\overset{CH_3}{C}}CH_2\cdot+\underset{B}{CH_3\overset{}{\underset{O}{\underset{\|}{C}}}CH_2\underset{H}{\overset{CH_3}{C}}\sim} \qquad (12)$$

Ketone A probably causes a 1718-cm^{-1} ir absorption band, and ketone B a 1726-cm^{-1} band.[8] Scission by reaction 11 will produce equimolar yields of ketone A and $CH_3\cdot$ reaction products (CH_4, C_2H_6, and possibly CH_3OH). Only trace amounts of methane (<0.02%) can be expected to occur in the volatile products, due to secondary photolysis of the main carbonyl products.[8] The total (CH_4 + C_2H_6 + CH_3OH) yield found during hydroperoxide photolysis was, however, usually ~10%. (In the example shown in Table I, this yield was unusually low.) This observed $CH_3\cdot$ reaction product yield agrees quite well with the average yield of ketone A (about 15% of the photolyzed hydroperoxide, Table II), since some $CH_3\cdot$ are probably scavened by alkoxy and peroxy radicals to give, respectively, ethers and peroxides.

The ketones A and B were found to be formed in quite similar yields during polypropylene hydroperoxide photolysis (Table II). From a comparison with well-characterized β-scission reactions in solution, the scission of polymeric alkoxy radicals by reaction 11 is unexpectedly efficient in comparison with reaction 12, since scission normally occurs at the weaker C–C bond, and yields the most stable alkyl radical.[4] For example, the rate constant for alkyl radical elimination from *t*-alkoxy radicals in solution at 25° can be estimated to be $\sim 2 \times 10^4$ sec^{-1} for $(CH_3)_2CHCH_2\cdot$, but only $\sim 2 \times 10^2$ sec^{-1} (or smaller) for $CH_3\cdot$.[3,4] In comparison, the rate constant for *t*-H abstraction from branched alkanes by *t*-butoxy radicals can be estimated to be $\sim 2.5 \times 10^3$ M^{-1} sec^{-1}.[3,26] The anomalous β-scission products and the low alcohol yield from the photolysis of polypropylene hydroperoxide indicate that the reactivity of polymeric alkoxy radicals in the solid phase is markedly different from the reactivity of alkoxy radicals in solution.

In the presence of hydroperoxides, the β-scission reaction (12) is probably the major source of backbone scission during the photodegradation of polypropylene, since approximately 15% of the photolyzed hydroperoxide groups undergoes this reaction. Unfortunately, the exact molecular weight distribution of the oxidized polymer and distribution of hydroperoxide groups is not known. Consequently, a quantitative comparison with the observed decrease in intrinsic viscosity on irradiation cannot be made.

The trace of acetol (0.1%) detected during hydroperoxide photolysis (Table I) probably arises from successive β scissions of 1,3-hydroperoxide groups, in the presence of $\cdot OH$ radicals. A similar decomposition has been reported to occur during the thermal oxidation of ethylene–propylene copolymers.[27] Some acetone may also be formed by successive β-scission reactions, followed by hydrogen abstraction steps. The experimental acetone yield (Table I) is, however, in fair agreement with the yield calculated from the quantum yield for ketone B photolysis. The low yield of olefins detected by glpc analysis shows that unzipping of alkyl macroradicals[28] does not occur at room temperature. Very similar quantitative yields of hydrocarbon volatiles (Table I) were reported during the thermal decomposition of polypropylene hydroperoxide.[7a]

The self-reaction of peroxy radicals expected from reaction 7 will result in the formation of inter- and intramolecular tetroxide intermediates.[29] The tetroxide may then decompose to generate alkoxy radicals and

$$RO_2\cdot + RO_2\cdot \rightleftharpoons [ROOOOR] \longrightarrow RO\cdot + O_2 + RO\cdot \qquad (13)$$

molecular oxygen. Since little O_2 was detected in the photolysis products, reaction 13 probably does not occur to any great extent during polypropylene hydroperoxide vacuum photolysis. However, the low O_2 yield may also be explained by efficient O_2 scavenging by the alkyl radicals produced during β scission. The peroxide yield detected after complete hydroperoxide photolysis may arise from RO· + RO· combination, or from alkyl·–$RO_2\cdot$ combination. From a consideration of the expected uv absorption of alkyl peroxides

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(Figure 1) and the low RO–OR bond strength (~37 kcal mol^{-1} [30]) peroxide photolysis to give alkoxy radicals can be expected to occur with a quantum yield close to unity, as was found in the gas phase photolysis of di-*t*-butyl peroxide.[31] This may mean that the residual peroxides are peresters or peracids, which will probably have even lower uv absorptions at 3650 Å than *t*-butyl hydroperoxide.

During photooxidation of many polypropylene films, a broad absorption extending from 1300 to 1000 cm^{-1} was observed at high degrees of oxidation. This was probably caused by a combination of ether and C–C, intra- or intermolecular cross-links, and epoxide formation. Similar ir changes in oxidized polyethylene have been attributed to ether formation.[32] Ether and epoxide formation probably accounts for some (<15%) of the alkoxy radicals produced in polypropylene photolysis under vacuum.

Photolysis of polypropylene hydroperoxides either in a sealed system (*i.e.*, in the presence of gaseous reaction products) or under a low pressure of hydrogen showed the formation of more alcohol and peroxide than photolysis during continuous evacuation (Table II). This was probably caused by alkoxy radical combination with, or H abstraction from, gaseous photolysis products. The apparent smaller intrinsic viscosity decrease during irradiation under hydrogen as compared with irradiation during continuous evacuation also indicates that less alkoxy radical β scission occurs in the presence of photolysis products. Gel formation was not detected in any of the photolyzed film samples.

Polypropylene Hydroperoxides and Polypropylene Photostability. Polypropylene processing (molding or extrusion) is usually carried out at 200° or greater.[33] At these temperatures, in the presence of atmospheric oxygen, hydroperoxide formation probably occurs, although the temperature instability of all hydroperoxides precludes the buildup of a significant stationary peroxide concentration in the polymer. The major oxidation products under processing conditions can be expected to be carbonyl derivatives, which result from the thermal decomposition of hydroperoxides.[8] Nevertheless, trace amounts of hydroperoxides probably exist in all processed polypropylene articles, despite the inclusion of antioxidants and peroxide decomposers in the commercial resin. In the presence of oxygen, the uv spectra of hydrocarbons are known to shift markedly toward higher wavelengths, due to the formation of O_2–hydrocarbon charge-transfer (C-T) complexes.[34] For alkane–O_2 C-T complexes, the uv absorptions extend well out toward 3000 Å, and Chien has proposed that the uv photooxidation detected in carefully purified alkanes at 3130 Å is initiated by free radicals formed during the absorption of uv by these C-T complexes. Obviously, if a similar C-T complex can be formed between polypropylene and O_2, slow initiation of photodeterioration might occur in regions of high O_2 concentration, such as exposed film surfaces, to give hydroperoxides as the first stable product.

The photolysis mechanism of polypropylene hydroperoxides under high vacuum may well be little different from photooxidation in air, since the polymer has a low O_2 permeability and a low dissolved oxygen content. This expected similarity is substantiated by the experimental observation that the distribution of carbonyl products found in a film sample photooxidized at 3700 Å to the same total carbonyl concentration as shown in Table II is very similar to the distribution shown in Table II. The presence of oxygen molecules at the photolysis site will not prevent the competing β-scission reactions 11 and 12 although radical-induced hydroperoxide decomposition (reaction 7) may be more extensive, as compared with vacuum irradiation, since the low molecular weight photolysis products will not diffuse rapidly from the photolysis site. Similarly alkoxy reaction with gaseous photolysis products will also be enhanced. Since the hydroperoxide concentration increases continuously during photooxidation (*cf.* Figure 2), some alkyl radicals generated by β scission of RO· or by hydrogen abstraction by HO· and RO· must combine with O_2 to give peroxy radicals and then fresh hydroperoxide (by reaction 6) to sustain the autooxidation. Peroxy radical formation will probably be favored at low rates of photolysis (*i.e.*, low light intensity and low hydroperoxide concentration) when radical–radical reactions will be relatively infrequent.

The high quantum efficiency for hydroperoxide photolysis to generate several types of free radicals and to cause appreciable chain scission indicates that tertiary hydroperoxide photolysis is a key step in the acceleration, and possibly also in the initiation of the photodeterioration of polypropylene. In peroxide-free polypropylene, *i.e.*, polypropylene molded or extruded under carefully controlled conditions, photolysis of trace ketonic impurities[8] or oxygen–polypropylene charge-transfer complexes[34b] may produce alkyl radicals which can combine with oxygen and give the first hydroperoxide groups. Efficient protection of polypropylene from photodegradation is likely to be obtained only by preventing photolysis of polypropylene hydroperoxide. Hydroperoxide photolysis may be prevented either by the rapid nonradical destruction of the hydroperoxide groups formed during photooxidation, or by deactivation of uv excited hydroperoxide groups. Development of stabilizer systems which can completely prevent hydroperoxide photolysis will probably require the use of highly efficient energy transfer compounds capable of accepting energy from the excited hydroperoxide groups. Photostabilizer additives such as sulfides and phosphites act as hydroperoxide decomposers, and are already in wide commercial use.[35]

Acknowledgments. The authors are grateful for gifts of polypropylene from Chemcell Ltd. Celanese Fibers Division, from Eastman Chemical Inter-American Ltd., and from Hercules Inc. Fibers and Film Department.

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