will be applied to obtain an approximation for r_n. According to Jacobson and Stockmayer,[8a] the ratio of the number of rings of n units (R_n) to the number of chains of n units (C_n) is

$$R_n/C_n = BVn^{-5/2}/A \qquad \text{(II-5)}$$

where

$$B = [3/(2\pi\nu)]^{3/2}/2b^3 \qquad \text{(II-6)}$$

A is a parameter of the reaction conditions, V denotes the total volume of the system, ν is the number of chain atoms per unit, and b is the effective bond length.

Assuming a small extent of cyclization

$$r_n \sim R_n/C_n = BVn^{-5/2}/A = (B\mathrm{m}/A)(1/c)n^{-5/2} \qquad \text{(II-7)}$$

where c is the concentration of reactive groups of one of the reactants in moles per liter. Summation of r_n over all ring sizes yields

$$\sum_{n=1}^{\infty} r_n = (B\mathrm{m}/A)(1/c) \sum_{n=1}^{\infty} n^{-5/2} \qquad \text{(II-8)}$$

The infinite series

$$\sum_{n=1}^{\infty} n^{-5/2}$$

is a well-known Riemann ζ function which has the value of 1.341. For a given polycondensation system, all parameters may be combined to give

$$2\sum_{n=1}^{\infty} r_n = k/c$$

Substituting this value into eq II-4 yields Stockmayer's gel equation[2] modified to account for ring formation, *viz.*

$$(P_A P_B)_{\text{gel}} = (1 - k/c)^{-1}(f_e - 1)^{-1}(g_e - 1)^{-1} \qquad \text{(II-9)}$$

The Photodegradation of Polypropylene Films. II. Photolysis of Ketonic Oxidation Products[1,2]

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Received June 17, 1969

ABSTRACT: Oxidation products can be expected to be inadvertently produced during the processing of polypropylene. In order to study the nature and photolytic mechanisms of these products, polypropylene films were prepared from resin which had been extensively air oxidized at 225° for various times. These films were then degraded under vacuum by irradiating at various wavelengths in the region 2200–3800 Å. Photolytic changes in the oxidized film samples were followed by glpc and ir analysis, and by film weight loss. The ir spectra of the air-oxidized films were compared with the ir spectra of model compounds related to polypropylene. From this comparison, and a consideration of the changes detected in the oxidized films during irradiation, the main oxidation products were believed to be the polymeric ketones $\sim CH(CH_3)CH_2C(=O)CH_2CH(CH_3)\sim$ (A) and $CH(CH_3)CH_2C(=O)CH_3$ (B). A study of the ir changes and the composition of the volatile products produced during irradiation indicated that ketone A is photolyzed primarily by a Norrish type I scission to give carbon monoxide and two macroradicals, whereas ketone B is photolyzed by a Norrish type II scission to give acetone and an unsaturated polymer chain end. The quantum yield for each photolytic reaction was determined from measurements of ir change and weight loss at various irradiation times. Both quantum yields were found to be approximately 0.08. The Norrish type I cleavage of ketones A and B is believed to be a possible source of initiation in the very early stages of the photooxidative deterioration of polypropylene. In later stages of deterioration, however, the photooxidation is probably dominated by other initiation steps, such as hydroperoxide photolysis.

Polypropylene has found wide commercial application in the form of fibers and films, despite the problems of thermal and photooxidative instability associated with this polymer. A partial solution of these problems has been achieved by the development of many ultraviolet (uv) stabilizers and antioxidant systems for use with polypropylene.[3] However, relatively little basic research has been published on the complex interplay of competing chemical reactions and physical effects involved in the photooxidative deterioration of the solid polymer. "Pure" saturated polyolefins are not expected to show a uv absorption beyond 2000 Å[4] and consequently should be indefinitely stable to the sunlight transmitted by the atmosphere (wavelengths greater than 2900 Å). However, any impurity in polypropylene which has a uv absorption extending to greater than 2900 Å will be a potential cause of photodegradation on exposure of the polymer to sunlight. Uv stabilizers protect polypropylene by screening the incident radiation from the chromophoric impurities as well as by energy transfer from the chromophores to the stabilizer.[5] It is essential that the nature, electronic absorption spectrum, and primary photolytic process of potential chromophoric impurities

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(1) N.R.C.C. No. 11,009.

(2) Previous paper in this series: Y. Kato, D. J. Carlsson, and D. M. Wiles, *J. Appl. Polym. Sci.*, in press.

(3) See, for example, J. E. Bonkowski, *Textile Res. J.*, **39**, 243 (1969).

(4) R. H. Partridge, *J. Chem. Phys.*, **45**, 1679 (1966).

(5) (a) P. J. Briggs and J. F. McKellar, *J. Appl. Polym. Sci.*, **12**, 1825 (1968); (b) A. P. Pivovarov and A. F. Lukovnikov, *Khim. Vysokikh Energii*, **2**, 220 (1968).

associated with polypropylene be investigated to aid the logical development of improved stabilizer systems.

The photo- and thermal oxidations of polypropylene have been shown to involve (at least in part) the conventional free-radical autoxidation chain process,[2,6] to give hydroperoxides as initial products. In addition a host of carbonyl products is also formed, probably by secondary processes.[2] The formation of oxidation products (particularly of the carbonyl type) during processing has frequently been cited as a possible cause of uv absorption and as the primary source of instability of polyolefins to near-uv radiation.[3] The present paper deals with the nature of the carbonyl products formed by thermal oxidation during simulated extrusion or molding conditions, together with the photolytic reactions of these products. The photolysis of carbonyl oxidation products was studied under vacuum in order to prevent the complicating reaction of oxygen with free-radical intermediates or activated species.

Experimental Section

Materials. All film samples were prepared from a predominantly isotactic, unstabilized polypropylene resin (Hercules Profax 6801). Before molding, this resin had an intrinsic viscosity of 5.59 dl g^{-1} and a viscosity average molecular weight of 1.5×10^6.

Film Preparation. Weighed amounts of the powdered polymer were sieved onto quartz plates (5 cm × 5 cm, 0.15 mm thickness) to give a uniform covering. The plates were then heated in air on a preheated hot plate at a temperature of 225 ± 5°, measured by a thermocouple embedded in the hot plate. After this controlled air oxidation (ranging from 1 to 5 min) each melted sample was capped with a second quartz plate, and the quartz–polymer–quartz composite was plunged into a methanol/Dry Ice mixture. These composites were then transferred to a nitrogen-filled glove box which contained a small hydraulic press. The composites were stored in the glove box for 24 hr before squeezing at 50–250 psi in the hydraulic press which had been preheated to 225°. The composites were then immediately quenched in methanol/Dry Ice. The oxidized polymer films were carefully stripped from the quartz, before vacuum drying. This procedure gave film samples of high optical clarity and of controlled, reasonably uniform thickness, ranging from 15 to 130 μ. Unoxidized film samples were also formed by melting polypropylene powder at 225° between quartz plates in the nitrogen-blanketed hydraulic press described above. These plates were squeezed at 125 psi, before quenching in methanol/Dry Ice mixture. Some of these films were then subjected to photooxidation in air, under a Hanovia lamp. The photooxidation conditions have been described previously.[2]

Film Characterization. Viscometry. Intrinsic viscosities $[\eta]$ of the polypropylene samples were determined by dilution viscometry at 135° in decalin. The technique will be described elsewhere.[7] Viscosity average molecular weights ($\bar{M}_v$) were calculated from the expression of Westerman.[8]

Infrared Analysis. Infrared (ir) spectra of each film sample were recorded with a double beam grating spectrometer (Beckman IR 8) fitted with a scale expansion unit, and a 10-in. slave recorder. Ir spectra were recorded by direct transmission, or by multiple attenuated total reflection (ATR), using a Wilks No. 9 ATR unit (25 reflection, KRS-5 crystal). Troublesome interference peaks in the transmission spectra of certain film samples were eliminated by mounting each film between two NaCl plates, with 1 drop of Nujol or isooctane on each side of the film. The absorbance of the relatively weak 2720-cm^{-1} polypropylene band was used as a convenient measure of film thickness. The 2720-cm^{-1} absorbance was calibrated against films of known thickness, determined by micrometer (using a controlled anvil pressure) or by weighing known areas of film.

Ir Band Assignments. Tentative assignments and estimation of extinction coefficients of the component peaks in the ir spectra (1800–1650-cm^{-1} region) of oxidized polypropylene films were made by comparison with the spectra of solutions of model compounds in isooctane or 2,4-dimethylpentane. Extinction coefficients for the model compounds were calculated from absorbances (based on peak heights) measured at low concentrations (<0.1 *M*) in 0.01-cm path cells. Peak maxima were accurately located by reference to water vapor bands. Results obtained for the model compounds are shown in Table I. Marked solvent shifts can be expected for certain absorptions in this region of the ir spectrum.[9] Nevertheless good agreement was found between the peak maxima given by the IR 8 spectrometer, and the values quoted by Rugg, *et al.*,[10] for solid solutions in polyethylene. Extinction coefficients were found to differ somewhat, however, and only experimental values determined on the IR 8 in solvents related to polypropylene have been employed in this paper.

Complex envelopes of overlapping carbonyl absorptions were frequently found in the ir spectra of oxidized poly-

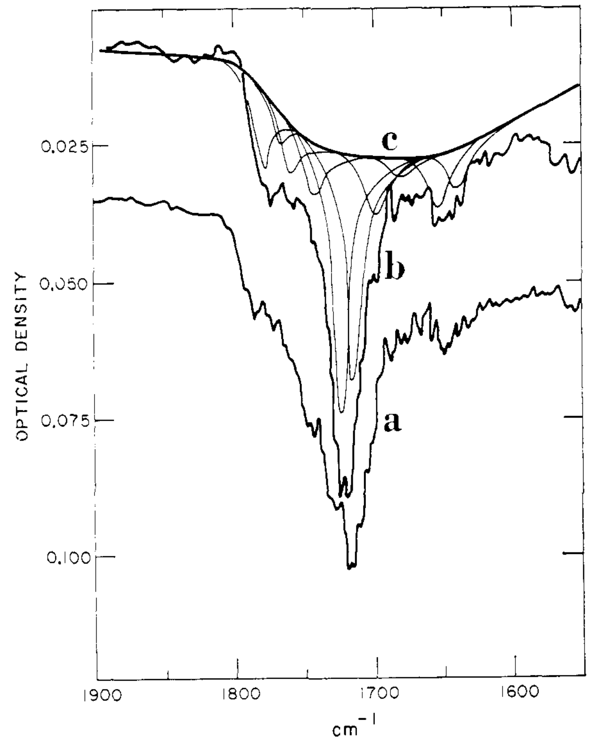

Figure 1. Carbonyl absorptions of oxidized polypropylene films: A, photooxidized 3700 Å, 200 hr, 40 μ thickness; B, melt oxidized at 225° in air, 37 μ thickness; C, component Lorentzian curves for B.

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(6) (a) L. Dulog, E. Radlman, and W. Kern, *Makromol. Chem.*, **60**, 1 (1963); **80**, 67 (1964); (b) C. R. Boss and J. C. W. Chien, *J. Polym. Sci., Part A-1*, **4**, 1543 (1966).

(7) D. J. Carlsson and D. M. Wiles, to be published.

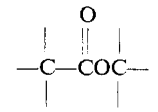
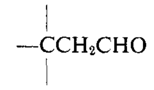
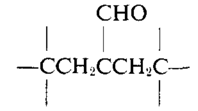
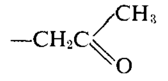
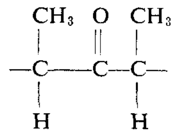
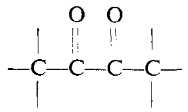
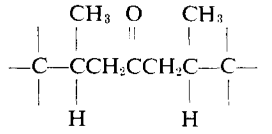
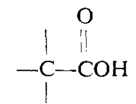
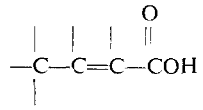
(8) L. Westerman, *J. Polym. Sci., Part A-1*, **1**, 411 (1963).

(9) K. J. Morgan and N. Unwin, *J. Chem. Soc., B*, 1336 (1967).

(10) F. M. Rugg, J. J. Smith, and R. C. Bacon, *J. Polym. Sci.*, **13**, 535 (1954).

TABLE I

IR ABSORPTION MAXIMA, AND EXTINCTION COEFFICIENTS OF SOME MODEL CARBONYL COMPOUNDS[a]

Compound	Carbonyl type	λ_{max},[b,c] cm^{-1}	ϵ,[b] $M^{-1}\ cm^{-1}$
Methyl *n*-butyrate Ethyl acetate	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{O}{\overset{\Vert}{C}}O\overset{\vert}{\underset{\vert}{C}}-$	1746 (1748–1738)	450
n-Dodecanal	 $-\overset{\vert}{\underset{\vert}{C}}CH_2CHO$	1736 (1733)	155 (170)
2-Ethylhexanal	 $-\overset{\vert}{\underset{\vert}{C}}CH_2\overset{CHO}{\overset{\vert}{C}}CH_2\overset{\vert}{\underset{\vert}{C}}-$	1733	155
2-Methyl-4-pentanone 2-Undecanone	 $-CH_2C(=O)CH_3$	1726 (1725)	300 ± 30
2,4-Dimethyl-3-pentanone 3-Pentanone	 $-\overset{CH_3}{\underset{H}{C}}-\overset{O}{\overset{\Vert}{C}}-\overset{CH_3}{\underset{H}{C}}-$	1724	300 ± 30
2,3-Heptanedione	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{O}{\overset{\Vert}{C}}-\overset{O}{\overset{\Vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$	1718	300
2,6-Dimethyl-4-heptanone 2,6,8-Trimethyl-4-nonanone	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{CH_3}{\underset{H}{C}}CH_2\overset{O}{\overset{\Vert}{C}}CH_2\overset{CH_3}{\underset{H}{C}}-\overset{\vert}{\underset{\vert}{C}}-$	1717 (1721)	300 ± 30 (220)
Octanoic acid	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{O}{\overset{\Vert}{C}}OH$	1712 (1713)	680 (530)
Methacrylic acid	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{C}=\overset{\vert}{C}-\overset{O}{\overset{\Vert}{C}}OH$	1700	660

[a] Determined in isooctane or 2,4-dimethylpentane solution. [b] Figures in parentheses refer to ref 10. [c] Accuracy ±1 cm^{-1}.

propylene films. These envelopes were plotted in terms of absorbance and resolved into their component peaks by the use of a Du Pont 310 curve resolver. The Du Pont 310 is basically an analog computer which can be programmed to generate several predetermined mathematical functions at desired relative positions. These functions may be displayed either individually or as the sum of all of the components. The absorption bands recorded by an ir spectrometer have been reported to be Lorentzian curves, modified in a Gaussian fashion by the spectrometer slit system.[11] However, isolated carbonyl absorption bands produced by the IR 8 spectrometer for simple ketones (~1722 cm^{-1}) were found to be simulated reasonably well by a single skewed Lorentzian function of 14 cm^{-1} half-band width. Complex carbonyl spectra were then resolved on the curve resolver by generating these functions at known (or expected) peak frequencies, and varying the height of individual peaks until the best approximation to the total ir envelope was obtained. A typical example is shown in Figure 1(b). Obviously choice of the base line (c) across the absorption envelope will have a marked effect on absolute heights determined for the component peaks. However, measurements of changes in peak height with time were usually required, and these were derived from spectra fitted to a common base line.

Owing to the small differences in ir frequency for differing types of carbonyl groups, chemical identification of the absorptions detected in oxidized film samples was also attempted by the following techniques. The carboxylic acid peaks are readily isolated at 1708–1710 cm^{-1} by the SF_4 treatment of Heacock.[12] This treatment causes complete conversion of $-C(=O)OH$ to $-C(=O)F$ which has a distinctive absorption at 1840 cm^{-1}, with a corresponding loss of the carboxylic acid absorption. Immersion of air-oxidized film samples for 24 hr in dilute nitric acid, or acidic dichromate produced no change in the ir spectra of the samples. This indicated the presence of little aldehyde, or failure to react in the solid phase. Similarly aqueous ammonia, or bisulfite and gaseous methyl mercaptan, had no apparent effect on the oxidized films. Alkaline hydroxylamine and anhydrous methanolic hydrochloric acid both caused marked reductions in the 1730–1715-cm^{-1} region

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(11) J. Pitha and R. N. Jones, *Can. J. Chem.*, **45**, 2347 (1967).

(12) J. F. Heacock, *J. Polym. Sci.*, 7, 2319 (1963).

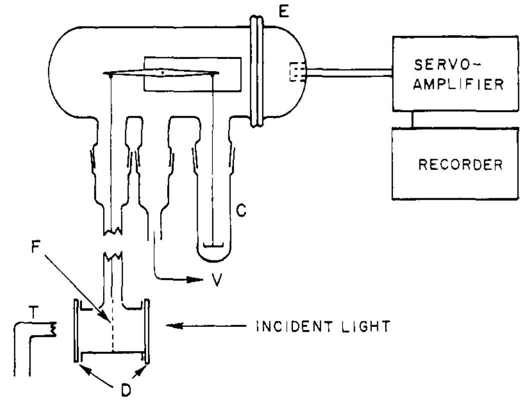

Figure 2. Vacuum microbalance.

of the ir. This indicated oxime and acetal/ketal formation, as an absorption at ~3400 cm^{-1} (-OH, -NH) was found in both cases, together with an extremely weak C=N absorption at about 1650–1670 cm^{-1} from the oxime(s). Film treatment with warm periodic acid caused no change in ir spectra, indicating the absence of 1,2-dione groups.

Vacuum Degradation Kinetics. Oxidized film samples (~12 cm^2) were impaled on a Nichrome frame, and suspended from the beam of a Cahn RG electrobalance, which was enclosed in a vacuum bottle as shown in Figure 2. The vacuum bottle (E) was rigidly clamped to a massive angle iron frame to minimize the vibration problems associated with balance operation at high sensitivities. Rates of weight change as low as 1 μg/hr were frequently measured, with an accuracy of ±10%. Each film sample (F) was arranged to hang in the center of a cylindrical cell fitted with quartz demountable windows (D). The film was positioned perpendicular to the beam from a super pressure mercury lamp (Osram HBO 200 W or HBO 500 W), which was collimated with two 8-cm diameter quartz condenser lenses to give a parallel beam of about 6 cm diameter. This beam passed through 10 cm of distilled water in a quartz cell (maintained at ~30° by external water cooling) and then through one of the optical filter systems listed in Table II. Forced air cooling of the filters was essential with 500-W lamp to prevent thermal breakage. The spectral energy distributions of the two mercury lamps are similar, and are shown in Figure 3. Irradiations were also carried out with a Bausch and Lomb high-intensity monochromator, fitted with an Osram HBO 200-W source. The divergent beam from the monochromator was collimated by quartz lenses to give a parallel beam of ~5 cm diameter. In both cases beam intensities were monitored several times during an irradiation by a calibrated thermopile, T (Eppley, 12 junction, quartz window), placed behind the cell. The thermopile indicated a fairly uniform intensity across the cross section of the light beams (variation less than ±10%). Intensities measured behind the cell were related to the true incident intensity on the film sample by a constant factor, which was determined from thermopile readings taken in blank experiments. Weight changes during irradiation of a film were displayed on a Hewlett-Packard 7127A recorder, at a chart speed of 1.5 in./hr. During irradiation, and for at least 3 hr prior to irradiation, the whole apparatus was continuously evacuated at ≤10^{-5} mm through outlet V by a mercury-free pumping system. A thermocouple indicated that the cell was maintained at 30 ± 2°, by the irradiating beams.

Table II

Optical Filters Used in the Irradiation of Polypropylene[a]

Filter	Filter type	Transmission (max.) Å	%	Half-band width, Å
A	Full arc	2200	100	
B	Corning C.S. no. 7-54	3300	88	~1340
C	Baird Atomic, interference	2477	24	296
D	Baird Atomic, interference	3026	18	160
E	Baird Atomic, interference	3313	24	200
F	Corning C.S. no. 7-54 + no. 0-52	3750	54	350

[a] Water-filled, ir filter used in all irradiations.

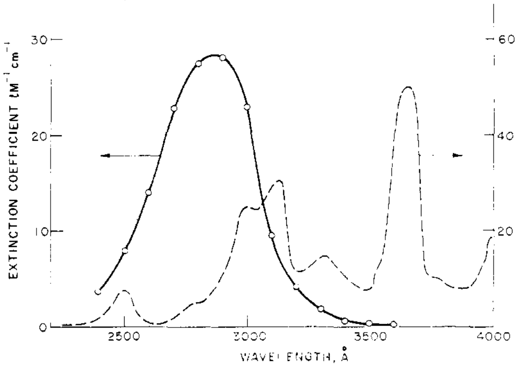

Figure 3. Uv output of source, and ketone uv absorption: – – – – – –, Osram SP200 mercury lamp; ———, uv absorption of branched ketones.

Volatile Product Analysis. The volatiles evolved during vacuum irradiation were collected by irradiating films of known weight (~0.020 g) in a rectangular quartz cell (Pyrocell, 13 × 13 × 45 mm). This cell was connected to two capsules, one of which was cooled in liquid nitrogen throughout the irradiation. Both capsules were equipped with glass dome break seals. Prior to irradiation, the apparatus was evacuated at 10^{-5} mm under mercury-free conditions for about 3 hr, and then sealed off. After irradiation, the two capsules were also sealed off. The contents of the capsule of condensable products were transferred under vacuum to a Pyrex U tube, which was subsequently coupled to the gas sampling valve (Hewlett-Packard 19048A) of a Hewlett-Packard 5750 gas chromatograph equipped with both flame-ionization and thermal-conductivity detectors (split ratio 5:1 in favor of the thermal conductivity detector). The U tube was heated to 100° immediately prior to injection. Condensable products were analyzed on a Porapak "R" column (Waters Associates Inc., 6 ft × $^3/_{16}$ in.), using a temperature-programmed sequence which allowed separation from CO_2 and C_2H_4 through to involatile organics such as methyl isobutyl ketone or propionic acid. The capsule containing noncondensable gases (CH_4, O_2, N_2, CO) was built into a Pyrex U tube so that the products could be admitted through the gas sampling valve of the gas chromatograph. Noncondensable gases were analyzed on a Molecular Sieve 5A column (Hewlett-Packard, 6 ft × $^3/_{16}$ in.) using a temperature-programmed sequence. Total gas evolution was estimated from the capsule volume, and the total volume of the assembled apparatus. Products were identified by retention time. Because of the complexity of the condensable products, where possible identical product mixtures were compared on the Porapak "R" column, on a β,β^1-thiodipropionitrile column (6 ft × 0.25 in., 5% on

Anakrom AS), and on a mass spectrometer. All three analyses gave identical assignments to the major products (>95% of total product). However, identification of minor products, and quantitative estimation of the highly polar products (such as acetic and formic acids, and water) are not on such a firm experimental basis. The volatile products collected during irradiation of film samples in the sealed system described above were found to be identical with the products collected during the irradiation of a film in a continuously evacuated cell. This cell was evacuated through two U tubes in series. The tubes were respectively packed with glass beads and activated charcoal and cooled in liquid nitrogen throughout the irradiation. The U tubes were designed to fit the gas chromatograph injection valve, and were heated to 100° immediately prior to injection.

Uv Absorptions. Owing to the low uv extinction coefficient (ϵ) expected for most types of carbonyl groups (20–40 M^{-1} cm^{-1}) and the difficulty of differentiating between a true absorption and the increase in Rayleigh scattering with decreasing wavelength,[4] direct determination of uv extinctions on oxidized film samples proved impossible. (Calculated optical densities at ~2800 Å for the most highly oxidized film samples were of the order of 0.005.) Several branched ketones with structures similar to ketonic derivatives of polypropylene (2,6-dimethyl-4-heptanone, 2,4-dimethyl-3-pentanone, and 2-methyl-4-pentanone) were found to have very similar uv absorption curves in isooctane solution (λ_{max} 2850 Å, ϵ_{max} 28 ± 3 M^{-1} cm^{-1}). This type of absorption curve is shown in Figure 3, and was adopted as the basis for the estimation of the number of quanta absorbed by ketonic oxidation products. Ethylene–carbon monoxide copolymers have been reported to have ϵ_{max} of 26 M^{-1} cm^{-1} at 2900 A.[13]

Results and Discussion

Chemical Nature and Photolysis Mechanism of Oxidized Polypropylene. The procedure used in the preparation of melt-oxidized polypropylene films is analogous to the processing conditions frequently employed in the production of polypropylene fibers. These conditions include extrusion at high temperature (>200°) into air, followed by a rapid quench to 0° to produce the smectic modification of polypropylene.[14] Consequently air oxidation at 225° of unstabilized polymers can be expected to generate oxidation products similar to those present in much smaller but significant amounts in extruded fibers. In addition, the high-temperature oxidation generates a film of somewhat simpler composition than, for example, uv photooxidation. This is shown by a comparison of the ir transmission spectra shown in Figure 1 (curves a and b). The photooxidized sample shows a complex absorption in the 1800–1650-cm^{-1} region, which indicates the presence of several types of carbonyl groups. In addition, the photooxidized samples all show a broad featureless absorption at about 3400 cm^{-1} which is typical of hydrogen-bonded alcohol and hydroperoxide groups.[15] The melt-oxidized films show no detectable absorption at 3400 cm^{-1} and only differ from unoxidized films in the carbonyl region. These carbonyl ir absorptions are dominated by a doublet at 1726 and 1718 cm^{-1} which can be resolved into the component peaks shown in Figure 1 on the Du Pont curve resolver. By comparison with Table I, the carbonyl doublet observed in the oxidized films is probably due to two, or possibly three, different types of ketones. Chemical treatment of the oxidized films indicated the absence of 1,2-diones (1718 cm^{-1}), and aldehydes (~1735 cm^{-1}), and the presence of only traces of carboxylic acids (1710 and 1700 cm^{-1}). The doublet was, however, markedly reduced in intensity by treatment with alkaline hydroxylamine, or with anhydrous methanolic HCl, indicating ketonic groups.

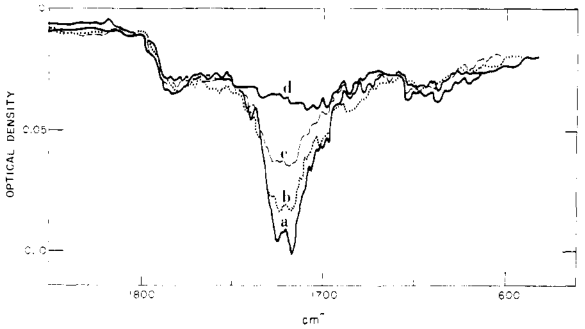

Figure 4. Ir changes during irradiation: total irradiation time (a) 0 hr, (b) 1.3 hr, (c) 3.2 hr, (d) 26.5 hr; irradiation with filter B, 4.3 × 10^{-4} kcal sec^{-1} on sample; film thickness 39 μ 0.0400 g.

The ratio of the optical densities (O.D.) of the 1726- and 1718-cm^{-1} peaks was found to be quite constant, despite variations in the extent of air oxidation of the films (O.D.$_{1726}$/O.D.$_{1718}$ = 1.22 ± 0.05). Extraction of the oxidized films with acetone or hexane (24 hr) had no effect on the ir spectra of the films. Consequently, the oxidation products are not low molecular weight species, and must be directly attached to the polypropylene backbone.

An initial rapid loss in weight, followed by a gradual decrease to constant weight was recorded when melt-oxidized film samples were suspended from the Cahn electrobalance under high vacuum and irradiated with any of the filter systems shown in Table II. Similar experiments in which irradiation with filter B (Table II) was periodically interrupted, and the film removed for ir analysis showed that the weight loss was accompanied by a decrease in the 1726- and 1718-cm^{-1} absorptions. Ir spectra recorded at several irradiation times are shown in Figure 4. Changes in weight with irradiation time are compared with the corresponding O.D. changes in Figure 5. Irradiation to constant

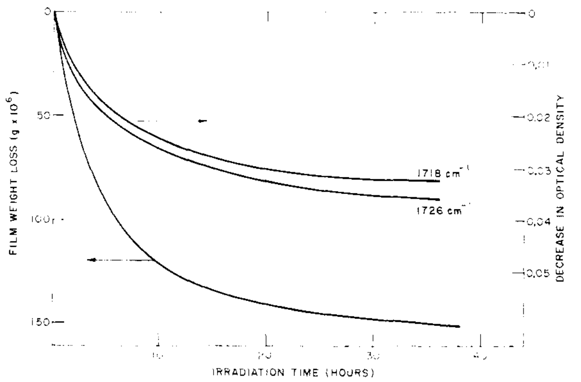

Figure 5. Changes in weight and ir during vacuum irradiation; irradiation conditions and film sample as in Figure 4.

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[13] G. H. Hartley and J. E. Guillet, *Macromolecules*, 1, 165 (1968).

[14] A. V. Galenti and C. L. Mantell, "Polypropylene Fibers and Films," Plenum Press, New York, N. Y., 1965.

[15] J. C. W. Chien, E. J. Vandenberg, and H. Jabloner, *J. Polym. Sci., Part A-1*, 6, 381 (1968).

Table III
Uv Irradiation of Oxidized Polypropylene.[a] Main Ir Changes and Volatile Products

	Sample A		Sample B	
	Mol × 10^6	Mol % of total volatiles	Mol × 10^6	Mol % of total volatiles
Oxidation product loss				
$[>C{=}O]_{1726\ cm^{-1}}$	1.89	60	0.90	51
$[>C{=}O]_{1718\ cm^{-1}}$	1.36	43	0.75	42
Total loss	3.25		1.65	
Volatile products collected				
CH_3COCH_3	1.54	49	0.83	47
CO	~1.1	34	~0.60	34
CO_2	~0.03	0.9	0.04	2.3
CH_3CHO	0.21	6.6	0.13	7.3
CH_3CH_2CHO	0.01	0.4	0.03	1.7
$CH_3CH(CH_3)OH$	0.05	1.5	0.01	0.5
$CH_3COCH_2CH_3$	0.03	0.9	0.02	1.1
CH_3COOH	0.04	1.4	0.02	1.1
$CH_3CH_2COCH_2CH_3$	0.03	0.9	0.01	0.5
C_3H_6	0.05	1.5	0.02	1.7
C_2H_6	0.05	1.5	0.03	1.7
C_2H_4	0.02	0.6	0.01	0.5
CH_4	0.06	1.8	0.01	0.5
Total volatiles	3.17		1.77	

[a] Irradiation with filter B, 0.5×10^{-4} kcal sec^{-1} on sample ~45 hr, 10^{-6} mm initially; weight of film samples = 0.0200 g; film thickness 38 ± 1 μ.

weight resulted in virtually complete loss of the 1726- and 1718-cm^{-1} absorptions.

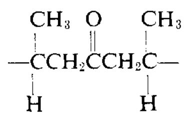
Collection of the volatiles evolved during irradiation with filter B showed that the major products from the oxidized films were carbon monoxide, and acetone. The glpc analysis of products from two films which had been melt oxidized to different extents and then irradiated to complete loss of the ketonic absorptions are shown in Table III. The main changes in film composition, based on the ir extinction coefficients for the ketones shown in Table I, are also given in Table III. Small decreases in absorbance at 1745 and 1785 cm^{-1} were occasionally detected. These changes are not included in Table III, as they amounted to less than 10% of the change in the ketone absorbances, and varied erratically from film to film. Products detected in only insignificant amounts (less than 0.4 mol % of the total product) include C_4H_8, C_4H_{10}, and isobutanal. Water, formaldehyde, formic acid, propane, and C_5, C_6, and C_7 hydrocarbons were not detected. Hydrogen was produced during irradiation, but was not quantitatively estimated. The CO_2 yield was irreproducible, and has been corrected for CO_2 desorption from the quartz cell. In several separate irradiations, volatiles were collected at varying extents of degradation of the ketone oxidation products. In each case, the composition of the volatiles was found to be independent of the extent of photodegradation.

Intrinsic viscosity [η] determinations before and after vacuum irradiation of oxidized film samples to constant weight indicated little change in viscosity average molecular weight[8] ($\bar{M}_v$). Thus, for a film oxidized to a similar degree to sample B (Table III) and irradiated under identical conditions

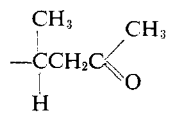
$$[\eta] \text{ before irradiation} = 0.63 \text{ dl g}^{-1};\ \bar{M}_v = 5.2 \times 10^4$$

$$[\eta] \text{ after irradiation} = 0.60 \text{ dl g}^{-1};\ \bar{M}_v = 4.8 \times 10^4$$

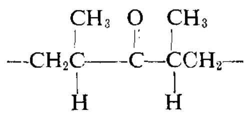
Based on the observed ir changes, and photodegradation products determined by glpc, it is possible to identify the main ketonic products of melt oxidation, and to differentiate between the possible photodegradative processes open to these uv chromophores. Direct formation of ketonic products can only result from thermal oxidation of the tertiary or secondary hydrogens in polypropylene. Ketones are most likely formed by the β scission of alkoxy radicals, generated in the high-temperature oxidation of polypropylene.[16] This oxidation can produce only three distinct types of ketones—A, B, and C. Comparison with Table I



A



B



C

indicates that, in the absence of diones, the 1718-cm^{-1} component of the ketone doublet is probably attributable to structure A. The ir assignments are not sufficiently definitive to indicate the origin of the 1726-cm^{-1} component, which can be attributed to B and/or C. The photolysis of low molecular weight ketones has been extensively studied, and the reactions involved are now well characterized.[17] The predominant processes are

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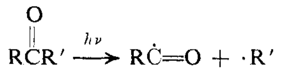
[16] J. v. Schooten and P. W. O. Wijga, *Soc. Chem. Ind.* (London) *Monographs*, No. 13, 432 (1961).

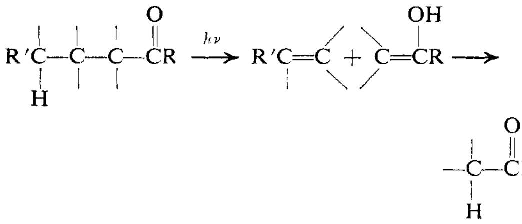
[17] J. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, Chapter 5.

Norrish type I process



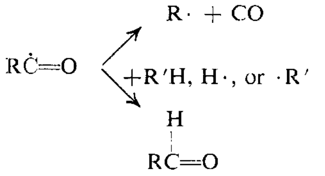
$$\mathrm{R\overset{O}{\overset{\|}{C}}R'} \xrightarrow{h\nu} \mathrm{R\dot{C}{=}O + \cdot R'} \qquad (1)$$

Norrish type II process



(2)

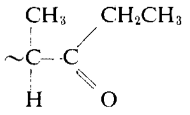
The acyl radical produced in (1) may subsequently decarbonylate to give an alkyl radical (R·) and CO (reaction 3). Alternatively the acyl radical may abstract a weakly bonded hydrogen, combine with atomic hydrogen (possibly produced during the photolysis of polypropylene), or disproportionate with ·R′[18] to give an aldehyde (reaction 4).



(3)

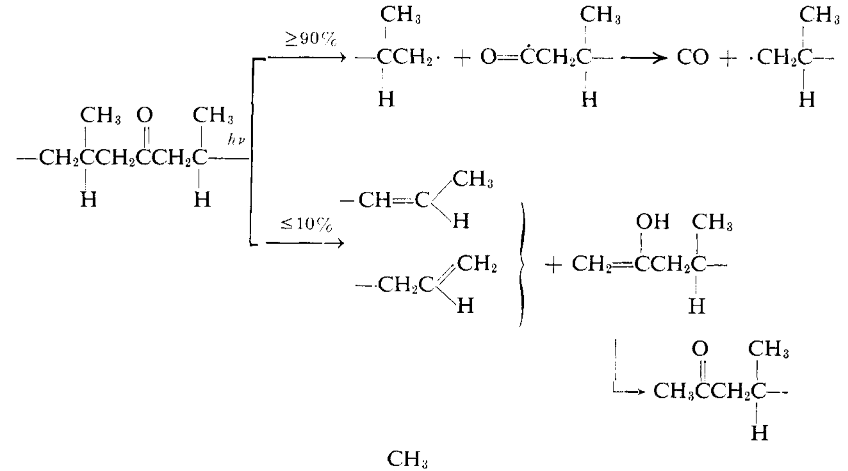
(4)

With filter B, ketones A, B, and C will all absorb some uv energy (*cf.* Figure 3) and can be expected to dissociate photochemically *via* reactions 1 and 2. Photolysis of ketone A will yield B and an unsaturated chain end (from reaction 2), and CO, R·, or a polymeric aldehyde (from reaction 1). Photolysis of B will yield acetone and unsaturation (from reaction 2) and CO, $CH_3\cdot$, or CH_3CHO (from reaction 1). Photolysis of C will produce a new polymeric ketone



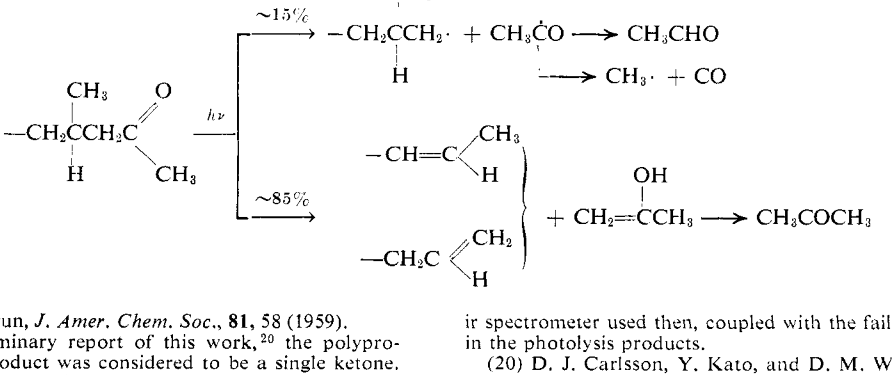
D

and unsaturation (from reaction 2) and R·, CO, or a polymeric aldehyde (from reaction 1). Ketone D can photolyze further to 3-pentanone and unsaturation (from reaction 2) and propionaldehyde or CO and $C_2H_5\cdot$ (from reaction 1). The immediate drop in the 1726-cm^{-1} absorption on irradiation (Figure 5) precludes reaction 2 (which will generate ketone B, and so contribute to the 1726-cm^{-1} absorption) as a significant step in the photolysis of A. Consequently, A must photolyze predominantly by a Norrish type I process to give two macroradicals and CO. Formation of long chain aldehydes by reaction 4 is excluded by the absence of change in the 1735-cm^{-1} ir absorption during irradiation. This leaves photolysis of B by a type II process as the sole source of acetone. Then from the correlation of the 1726-cm^{-1} peak with the glpc products (Table III), B must be the main component of the 1726-cm^{-1} peak, and the main decomposition of B is by a Norrish type II process. This is substantiated by the low CH_4 yield as compared with CO, since equimolar amounts of CO and CH_4 will be formed by a type I photolysis of ketone B. Ketone C is probably not formed in melt oxidation. The analytical results as a whole then indicate that the main photolytic processes of polypropylene melt oxidation products[19,20] are



(1A)

(2A)



(1B)

(2B)

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[18] K. F. Wissbrun, *J. Amer. Chem. Soc.*, **81**, 58 (1959).

[19] In the preliminary report of this work,[20] the polypropylene oxidation product was considered to be a single ketone. This conclusion was caused by the low resolution of the (prism) ir spectrometer used then, coupled with the failure to detect CO in the photolysis products.

[20] D. J. Carlsson, Y. Kato, and D. M. Wiles, *Macromolecules*, **1**, 459 (1968).

Table IV
Quantum Yields for the Photolysis of Polypropylene Ketones at 30°

Irradiation wavelength, Å	Exptl method	$(\Phi_A)^{NI}$	Quantum yield $(\Phi_B)^{NII}$	$(\Phi_A)^{NI} + 2.5(\Phi_B)^{NII}$	$\Phi_{A,B}$
3300 ± 670	(O.D.) change	0.070			
3300 ± 670	(O.D.) change		0.080		
3300 ± 670	Slope $\frac{\log(\Delta(\mu g)_\infty - \Delta(\mu g)_t)}{t}$				0.081
2477 ± 150	$(-d(\mu g)/dt)_{\text{initial}}$			0.37	0.10
3026 ± 80	$(-d(\mu g)/dt)_{\text{initial}}$			0.33	0.091
3300 ± 670	$(-d(\mu g)/dt)_{\text{initial}}$			0.41	0.11
3313 ± 100	$(-d(\mu g)/dt)_{\text{initial}}$			0.41	0.11
3750 ± 180	$(-d(\mu g)/dt)_{\text{initial}}$			0.34	0.095

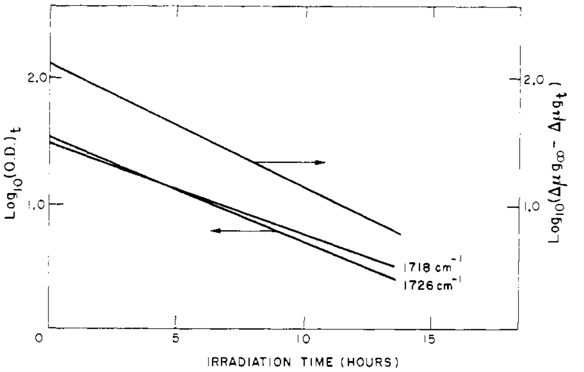

Figure 6. Changes in weight and ir during vacuum irradiation; irradiation conditions and film sample as in Figure 4.

The presence of CH_3CHO and CH_4 in the photolysis products indicates that some type I photolysis of ketone B does occur (reaction 1B). The ir data are insufficiently precise to exclude the occurrence of as much as 10% of the type II scission in the photolysis of ketone A.

Increasing ethylenic unsaturation (at ~1645 cm^{-1}) was detected during the vacuum irradiation of most film samples with filter B. Owing to the low >C=C< ir extinction (~20 M^{-1} cm^{-1} [10]) little quantitative information was derived from this change. The size of the absorbance increase at 1645 cm^{-1} was, however, consistent with extensive photolysis of ketone B by a reaction 2B. The complete type II photolysis of ketone B will produce an equivalent concentration of vinylene (with some vinyl[21]) unsaturation. Changes in ir absorbance at 964 cm^{-1} (vinylene) and 908 cm^{-1} (vinyl) were not detected due to the proximity of strong polypropylene ir absorptions (973 and 900 cm^{-1}). No significant change in >C=C< unsaturation at 1645 cm^{-1} was observed during the vacuum irradiation of unoxidized polypropylene films with filter B.

The presence of ketone A as a significant product in the high-temperature oxidation of polypropylene is somewhat unexpected. Solution decomposition of the common precursor to A and B (the *t*-alkoxy radical) usually occurs by β scission to give only a ketone similar to B. However, ketone A was also detected as a major product during the photolysis of polypropylene hydroperoxides. This topic is discussed in detail in the following paper (part III).

Kinetics of Photolysis of Oxidized Polypropylene.

Quantum yields for the main photolytic reactions of ketones A and B can be estimated from the changes in ir absorptions with irradiation time. For film samples with low uv absorptions, the O.D.–time curves for both types of ketone can be expected to follow first-order rate expressions of the type

$$\ln \frac{(\mathrm{O.D.})_t{}^{1718}}{(\mathrm{O.D.})_0{}^{1718}} = -2.303\Phi_A \frac{lt}{V} \sum_{\lambda_1}^{\lambda_2} I_\lambda \epsilon_\lambda \qquad (5)$$

where $(\mathrm{O.D.})_t{}^{1718}$ is the optical density at time t, $(\mathrm{O.D.})_0{}^{1718}$ is the initial optical density, and Φ_A the over-all quantum yield for loss of ketone A between the irradiation wavelength limits of λ_1 and λ_2, l and V are the sample thickness and volume, ϵ_λ the molar extinction coefficient for ketone A, and I_λ the incident light intensity (einsteins per second) on the sample at wavelength λ. Plots of log $(\mathrm{O.D.})_t$ against time were found to be linear (Figure 6) for both ketone types and the quantum yields for photolysis of each ketone were calculated from the slope of these plots. Experimental values for the over-all quantum yields are shown in Table IV. The integrated expression

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

was calculated from the known spectral power distribution of the mercury lamp, corrected for the transmission of the filter system of each wavelength, and the uv extinction coefficients here derived for model ketones in a polypropylene-like solvent (Figure 3). In all experimental determinations of quantum yields, the maximum uv absorption at any wavelength was less than 0.5% of the incident intensity. Since the analytical results indicate that only one dominant photolytic process is responsible for the loss of each of the ketones A and B, the over-all quantum yields calculated from eq 5 (Φ_A) can be taken to equal the quantum yield for type I scission of ketone A, $(\Phi_A)^{NI}$. Similarly the over-all quantum yield Φ_B is equal to the quantum yield for type II scission of ketone B, $(\Phi_B)^{NII}$. From Table IV it is apparent that the quantum yields for the two types of scission are equal within experimental error. This equality was also indicated by the fact that the plots of weight loss against the O.D. of each ketone are linear.

An approximate value for the quantum yield $(\Phi_B)^{NI}$ for the Norrish type I photolysis of ketone B (see reaction 1B above) can be calculated from the ratio of

(21) P. Ausloos, *J. Phys. Chem.*, **65**, 1616 (1961).

TABLE V
WEIGHT LOSS DATA AT VARIOUS FILM THICKNESSES AND DEGREES OF OXIDATION[a]

Film thickness, μ	$[\mathrm{CO}]_{\mathrm{total}}$,[b] M	$(-\mathrm{d}(\mu\mathrm{g})/\mathrm{d}t)/[\mathrm{CO}]_{\mathrm{total}}$,[c] μg mol^{-1} sec^{-1} $\times 10^{-3}$	Total weight loss/$[\mathrm{CO}]_{\mathrm{total}}$, g/mol
16	0.066	4.9	51
24	0.073	5.3	55
31	0.123	5.2	57
33	0.089	4.7	48
36	0.065	5.3	50
40	0.025	5.0	46
57	0.062	4.0	52
92	0.026	3.2	54
112	0.034	2.2	33
122	0.031	3.4	62

[a] Irradiation with filter A, 10^{-6} mm, intensity $\backsim 1.0 \times 10^{-4}$ kcal sec^{-1} on sample. [b] $[\mathrm{CO}]_{\mathrm{total}}$ = [ketone A] + [ketone B]. [c] Measured at the start of irradiation.

(acetaldehyde + methane) to acetone estimated by glpc (*cf.* Table III). Then

$$(\Phi_{\mathrm{B}})^{\mathrm{NI}} \simeq \frac{[\mathrm{CH_3CHO}] + [\mathrm{CH_4}]}{[\mathrm{CH_3COCH_3}]}(\Phi_{\mathrm{B}})^{\mathrm{NII}} \simeq 0.013$$

Since the composition of the volatile products is known, the weight loss–time curves produced by the electrobalance can also be used in the derivation of quantum yields. Meaningful values will only be obtained, however, if the escape of volatiles by diffusion to the film surfaces is fast in comparison with the rate of generation of products in the bulk of each film. Measurements of the initial rate of weight loss ($-\mathrm{d}(\mu\mathrm{g})/\mathrm{d}t$ in micrograms per second) per mole of ketone in the sample, for the irradiation of films ranging in thickness from 16 to 122 μ are shown in Table V. For films greater than 60 μ with filter system A, the rate of weight loss appears to be limited by diffusion, but, below 60 μ, the rate is independent of the sample thickness. Since filter system A has a greater transmission than any other filter used, diffusion control of ($-\mathrm{d}(\mu\mathrm{g})/\mathrm{d}t$) will also be unimportant for films up to at least 60 μ in thickness under all other irradiation conditions. At constant film thickness ($\sim$35 μ), ($-\mathrm{d}(\mu\mathrm{g})/\mathrm{d}t$) was found to be directly proportional to the total ketone concentration in each sample (0.01–0.07 M) and to be directly proportional to the incident light intensity (6.6×10^{-5} to 0.06×10^{-5} kcal sec^{-1} on film sample, filter system B). Based on the constant ratio of ketone A to B in the oxidized polymer, and the product analyses which showed that the major volatiles produced from A and B are CO (reaction 1A) and acetone (reaction 2B), respectively, the factor (total weight loss)/(total initial ketone) is expected to be a constant. This factor is calculated to be 45 g/mol and is in fair agreement with the experimental values shown in Table V.

The concurrent first-order loss of ketones A and B will result in a rate of weight loss which may be described by the expression

$$-\mathrm{d}(\mu\mathrm{g})/\mathrm{d}t = 2.303 \times 10^{6}\, l \sum_{\lambda_1}^{\lambda_2} I_{\lambda}\epsilon_{\lambda}(M_{\mathrm{A}}\Phi_{\mathrm{A}} \times [>\mathrm{CO_A}]_t + M_{\mathrm{B}}\Phi_{\mathrm{B}}[>\mathrm{CO_B}]_t \quad (6)$$

where M is the weight change (grams) per mole of photolyzed ketone, and $[>\mathrm{CO}]_t$ the concentration of each ketone at time t. Since the ratio ($\mathrm{O.D.}_{1726}/\mathrm{O.D.}_{1718}$) was found to be a constant (1.22), and both ketones A and B have the same ir extinction coefficient (Table I), the ratio $[>\mathrm{CO_A}]/[>\mathrm{CO_B}]$ is also 1.22. If photolysis of A and B are assumed to be described by reactions 1A and 2B, then M_{A} = 28 g/mol and M_{B} = 58 g/mol. The use of the above constants and relationships allows the calculation of $(\Phi_{\mathrm{A}})^{\mathrm{NI}} + 2.5(\Phi_{\mathrm{B}})^{\mathrm{NII}}$ from eq 6. If $(\Phi_{\mathrm{A}})^{\mathrm{NI}}$ is taken to be equal to $(\Phi_{\mathrm{B}})^{\mathrm{NII}}$, as was found spectroscopically, the average quantum yield, $\Phi_{\mathrm{A,B}}$, derived from $(\Phi_{\mathrm{A}})^{\mathrm{NI}} + 2.5(\Phi_{\mathrm{B}})^{\mathrm{NII}}$ values can be compared directly with $(\Phi_{\mathrm{A}})^{\mathrm{NI}}$ and $(\Phi_{\mathrm{B}})^{\mathrm{NII}}$. Average quantum yields calculated from initial rates of weight loss at various wavelengths of irradiation and $[(\Phi_{\mathrm{A}})^{\mathrm{NI}} + 2.5\,(\Phi_{\mathrm{B}})^{\mathrm{NII}}]$ values are shown in Table IV. Based on the above assumptions it can also be shown that

$$\log\,(\Delta(\mu\mathrm{g})_{\infty} - \Delta(\mu\mathrm{g})_t) = \text{constant} - \Phi_{\mathrm{A,B}} \sum_{\lambda_1}^{\lambda_2} \mathrm{I}_{\lambda}\epsilon_{\lambda}\frac{lt}{V} \quad (7)$$

where $\Delta(\mu\mathrm{g})_{\infty}$ is the total weight loss observed, and $\Delta(\mu\mathrm{g})_t$ the weight loss observed at time t. Plots of $\log\,(\Delta(\mu\mathrm{g})_{\infty} - \Delta(\mu\mathrm{g})_t)$ against time were found to be linear (Figure 6) and the average quantum yield calculated from the slope of these curves is shown in Table IV. After complete loss of the volatile products from ketone degradation, a slow residual rate of weight decrease ($<3 \times 10^{-4}$ μg sec^{-1}) was found during the vacuum irradiation of most film samples. This was attributed to the slow photolysis of polypropylene itself (to give mainly $\mathrm{H_2}$), and to the photolysis of traces of other carbonyl products (acids, esters) present in the samples. A correction for this slow residual degradation has been applied over the complete weight loss–time curve before measurement of $\Delta(\mu\mathrm{g})_{\infty}$ and $\Delta(\mu\mathrm{g})_t$. A very slow hydrogen evolution, together with a small increase in the intrinsic viscosity of the film sample, was always detected during the irradiation of "pure" (*i.e.*, unoxidized, and unstabilized) polypropylene with filter B. The cause of these effects is not known but may stem from the photolysis of unsaturated impurities which absorb some of the shorter wave uv transmitted by the filter system.

Repeated quantum yield determinations during irradiation with a given filter system usually agreed within $\pm 15\%$. However, experimental quantum yields determined in different spectral regions (Table IV) cannot be expected to agree to better than $\pm 25\%$, since a small change in the assumed uv absorption maximum and extinction coefficients for polypropylene ketones results in an appreciable change in the integrated total absorption

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

Norrish type I and II processes have been reported during the photolysis of several polymeric systems, including poly(methyl vinyl ketone),[18,22] ethylene–

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[22] J. E. Guillet and R. G. W. Norrish, *Proc. Roy. Soc.* (London), A233, 153 (1955).

carbon monoxide copolymers,[13] and poly(*t*-butyl acrylate).[23] Ethylene–carbon monoxide copolymers give a Φ^{NII} of 0.025 in solid films.[13] However, the higher value of 0.080 for Φ^{NII} shown in Table IV for the polypropylene terminal methyl ketone (B) is not surprising in view of the reported sensitivity of the type II process to freedom of the polymer backbone.[13] The type II reaction proceeds through a six-membered cyclic intermediate which will be more readily formed by a terminal ketone than by long chain ketones similar to A. The quantum yield for the Norrish type II photolysis of ketone A is probably less than 0.010.

The value of 0.070 for $(\Phi_A)^{\text{NI}}$ and the approximate value of 0.013 for $(\Phi_B)^{\text{NI}}$ at 30° in polypropylene are much greater than the corresponding values estimated in the ethylene–carbon monoxide copolymer (about 0.003 at 25° in solution[13]). However, a value of 0.06 has been reported for poly(methyl vinyl ketone) films.[18] In the absence of intersystem crossing and fluorescence, the method of Reinisch and Gloria[24] allows the estimation of an approximate value of $(\Phi_A)^{\text{NI}}$ for reaction from the excited singlet state of polymers. The C—C=O bond dissociation energy has been estimated to be 80 ± 1 kcal mol^{-1} for primary, secondary, and tertiary substituted ketones.[25] Since the polymer C—C=O bond strength must be similar, the approximate quantum yield (Φ^{NI}) is calculated to be 0.06 at 30°. Quantum yields for the type I photolysis of a series of di-*n*-alkyl ketones in solution have been shown to decrease to a limiting value of 0.012 (at 120°) as chain length increases, and to be viscosity independent.[26] However, similar data are not available for branched ketones, and the theory of type I eliminations from excited ketones is insufficiently well developed to predict the dependence of quantum yields on molecular structure.

Unzipping of the alkyl macroradicals formed by the type I process does not appear to occur to any great extent at 30°, since only trivial yields of hydrocarbon products were detected during the photolysis of ketones A and B (Table III). Alcohol formation from electronically excited ketones may occur by cyclization of the type II intermediate to give a cyclobutane derivative[27] or by hydrogen abstraction from a neighboring chain.[28] Hydrogen abstraction has only been observed for aryl and aryl alkyl ketones. Alcohol formation was not detected by ir spectroscopy during the irradiation of the polypropylene ketones.

Since the type I photolysis of ketone A must lead to chain scission, the small change in intrinsic viscosity [η] (less than 10%) resulting from the photolysis of an oxidized film is somewhat unexpected. This phenomenon may be caused by a competing cross-linking reaction due to combination of the neighboring alkyl radicals produced in reaction 1A. Alternatively, a shift in molecular weight distribution is not necessarily accompanied by a change in [η]. In addition, polymer samples containing ketonic substituents cannot be expected to obey the same Mark–Houwink equation as the ketone-free polymer films produced on photolysis. The relationship of Westerman[8] is almost certainly invalid for the oxidized samples.

Polypropylene Ketones and Polypropylene Photostability. The ketonic products A and B can be expected to occur as trace amounts in "pure" polypropylene, and as components of the complex photooxidation products. Consequently photolytic reactions of these ketones may be important both in the very early stages of photodegradation, and in the sustenance of an established photodegradation reaction. The ketones may affect the course of the photodegradation by contributing to free-radical formation, chain scission, and energy transfer.

The ketone uv absorption at 2900 Å is caused by a n–π* transition in which a nonbonding electron is promoted to the first singlet (antibonding) π* orbital.[17] Decomposition by a type I or II process may occur from this level or the excited singlet may undergo intersystem crossing to the first triplet level (T_1). Chemical decomposition will also occur from T_1. Trozzolo and Winslow[29] have proposed that in the presence of oxygen, energy transfer may occur from the ketone triplet level to oxygen to form singlet oxygen $^1O_2$. Singlet oxygen may then react with neighboring vinyl groups to form polypropylene hydroperoxides, which will then rapidly photolyze and so initiate photodegradation.[30] However, oxygen has been found to show no quenching effect on the type II photolysis of ethylene–carbon monoxide copolymers.[13] This was attributed to the low solubility of O_2 in the polymer, and the short lifetime of the ketone triplet. Consequently any contribution to the instability of polypropylene by energy transfer from ketone to oxygen can be expected to be restricted to the surface of the film or fiber.

Type II dissociation of ketone B from the excited triplet or singlet level will cause the loss of a small molecule, and generate unsaturation. Any type II dissociation of A will result in chain scission, although further photolysis of the resultant ketone B will not contribute to degradation. Hence, apart from the initial photolysis to give volatiles and some chain scission, the Norrish type II scission of ketonic impurities is unlikely to accelerate significantly the photodegradation of polypropylene under weathering conditions. Type I photolysis of ketones A and B, however, will generate free radicals, and also cause chain scission in the case of A (reactions 1A and 1B). These alkyl radicals may either combine or disproportionate, and so cause no further immediate damage, or during irradiation in air, may combine with dissolved oxygen in the polymer to give peroxy radicals, $RO_2\cdot$.[6] The peroxy radical is the well-established intermediate in most thermal and photooxidations. Radical combination of the two macroradicals formed in reaction 1A

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(23) A. R. Monahan, *J. Polym. Sci., Part A-1*, **4**, 2381 (1966); 2333 (1967).

(24) R. F. Reinisch and H. R. Gloria, *Polym. Preprints*, **9**, 349 (1968).

(25) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

(26) G. H. Hartley and J. E. Guillet, *Macromolecules*, **1**, 413 (1968).

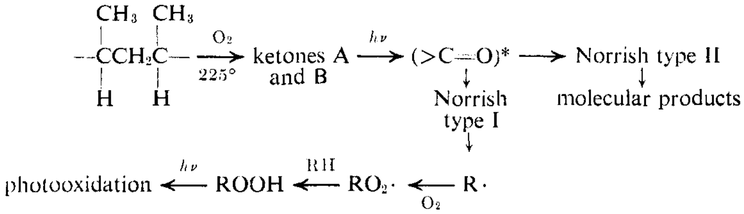
(27) N. C. Yang and D. D. H. Yang, *J. Amer. Chem. Soc.*, **80**, 2913 (1958).

(28) C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965).

(29) A. M. Trozzolo and F. H. Winslow, *Macromolecules*, **1**, 98 (1968).

(30) D. J. Carlsson and D. M. Wiles, *ibid.*, **2**, 597 (1969).

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



$$\begin{tikzcd}
 & \text{--}\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}\text{--} \arrow[r, "O_2", "225°"'] & \text{ketones A and B} \arrow[r, "h\nu"] & (>C{=}O)^* \arrow[r] \arrow[d] & \text{Norrish type II} \arrow[d] \\
 & & & \text{Norrish type I} \arrow[d] & \text{molecular products} \\
\text{photooxidation} & \text{ROOH} \arrow[l, "h\nu"'] & RO_2\cdot \arrow[l, "RH"'] & R\cdot \arrow[l, "O_2"] &
\end{tikzcd}$$

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.

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

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Received June 17, 1969

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

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

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).