

can also be expected to originate in their exposed surfaces and to be of great importance because of the high surface-to-volume ratio of fibers. In addition, the observation of polypropylene deterioration by ATR spectroscopy offers a practical accelerated test "for detecting the onset of photooxidation," as suggested by Chan and Hawkins.¹⁸

(18) M. G. Chan and W. L. Hawkins, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 9, 1638 (1968).

The origin of the surface photooxidation effect and its importance in the photodeterioration of polypropylene are discussed in detail in a following paper.⁸

Acknowledgments. The authors wish to thank the companies mentioned in the text for supplying polypropylene film samples and releasing processing data.

Photooxidation of Polypropylene Films. V. Origin of Preferential Surface Oxidation¹

D. J. Carlsson* and D. M. Wiles

Division of Chemistry, National Research Council of Canada, Ottawa, Canada. Received December 16, 1970.

ABSTRACT: The preferential surface photooxidation of many unstabilized commercial polypropylene films in air was found to originate from the presence of surface chromophores, such as $-\text{OOH}$ and $>\text{C}=\text{O}$, rather than from diffusion control of the degradation, or morphological effects. This was established by the use of attenuated total reflection and transmission infrared spectroscopy to determine the photooxidation product distribution within various uv-irradiated film samples. The oxidation of commercial film samples was compared with either uv or γ initiation, and was also studied under controlled O_2 diffusion conditions. After uv irradiation, specially prepared film samples showed either little surface oxidation (films pressed under a N_2 atmosphere) or enhanced surface reaction (films exposed to O_3 or an O_2 corona discharge prior to irradiation). The observed surface photooxidation of commercial films is believed to result from a limited thermal oxidation of the film surfaces during manufacture. The stability of various commercial films is compared and discussed in terms of the extrusion technique used in their manufacture and fluorescent emission spectrum of each sample. The relevance of the results both to the photostabilization and to the accelerated decomposition of polypropylene films is considered.

In the previous paper in this series,² unstabilized commercial polypropylene films were reported to undergo rapid photooxidative attack close to the film surfaces, while the bulk of each sample was largely undegraded. This effect was detected by the use of attenuated total reflection (ATR) spectroscopy in the infrared (ir) region, and was demonstrated to occur during the irradiation of many different film samples with various ultraviolet (uv) sources. Since this surface oxidation is sufficient to cause the brittle failure of a stressed film, a study of the origin of the phenomenon is of great importance, both in the development of uv stabilizer systems to extend the useful life of an article, and possibly also in the opposite problem of deliberately introducing "self-destruct" properties into packaging material to reduce environmental pollution.

The concentration of oxidation products (hydroperoxides, ROOH , and carbonyl derivatives, $>\text{C}=\text{O}$) close to the surfaces of films as compared with the bulk of each film during air photooxidation might arise from several physical and/or chemical effects. Possible causes may be arbitrarily divided into diffusion effects and kinetic effects. In a situation of uniform polymer reactivity, Wilson³ has concluded that a steep gas concentration gradient might become established close to the surfaces of a film during a film-gas reaction for certain values of diffusion and reaction constants. Similarly, diffusion effects might also arise from the buildup of a gaseous oxidation product in the film if this product is capable of inhibiting the polymer oxidation. In the absence of diffusion-controlled effects, possible kinetic effects include a high photoinitiation rate or enhanced polymer reactivity close to

the surface, or alternatively a lower rate of oxidative chain termination in the surface layer.

In this paper, the origin of the observed rapid surface photooxidation of polypropylene films is investigated by a comparison of the γ - and uv-initiated deterioration, by a study of O_2 diffusion effects, and by an investigation of the importance of various pretreatments on film stability. Product distributions within samples were determined by ATR and transmission infrared spectroscopy. The relative photostability of polypropylene films obtained from various commercial sources is also reported, and the observed differences are discussed.⁴

Experimental Section

Polypropylene Films. The manufacturer, extrusion method, thickness, and density of each of the commercial films studied are listed in Table I. None of the films was appreciably oriented, except the ICI sample. The films were initially extracted and dried as described previously.² Special films were prepared from an unstabilized polypropylene powder (Moplen, Montecatini Edison) under carefully controlled conditions.⁵ The powder was distributed over quartz plates, and these plates were stored under dry N_2 for several days. The powder was then pressed between quartz plates in the N_2 atmosphere at 250° to give $30\text{-}\mu$ films, which were immediately quenched in Dry Ice-methanol. The films were carefully stripped from the quartz and vacuum dried.

Ir Spectra. Transmission and ATR spectra of film samples were determined by the previously described methods.⁶ ATR spectra

(1) Issued as NRCC Report No. 11868.

(2) D. J. Carlsson and D. M. Wiles, *Macromolecules*, 4, 174 (1971).

(3) J. E. Wilson, *J. Chem. Phys.*, 22, 334 (1954).

(4) The results obtained with the commercial films used in this work should not be considered to endorse or discredit the products of any manufacturer. Many of the samples were experimental grades, or subjected to unusual treatments.

(5) Y. Kato, D. J. Carlsson and D. M. Wiles, *J. Appl. Polym. Sci.*, 13, 1447 (1969).

(6) D. J. Carlsson and D. M. Wiles, *Can. J. Chem.*, 48, 2397 (1970).

TABLE I
 POLYPROPYLENE FILM SAMPLES

Film	Manu- facturer	Extrusion process	Thick- ness, μ	Film density, g ml ⁻¹	Rel fluores- cence intensity ^a
A	Eastman	Chill roll cast ^b	22	0.8858	1.5
B	Enjay	Chill roll cast ^b	22	0.8888	5.0
C	Enjay	Blown ^{c,d}	22	0.8902	3.2
D	Shell	Blown ^{c,d}	22	0.8888	1.8
E	Phillips	Blown ^e	44	0.9026	2.1
F	ICI ^e	Chill roll cast ^b	14	0.9116	1.0

^a Excitation at 2950 Å, emission at 3450 Å at 25°. Relative to film F. ^b Extruded as a flat sheet onto a cooled roll. ^c Extruded as a tube from a circular die, and expanded by air pressure. ^d Water cooling used during extrusion of the tubular film. ^e Biaxially oriented.

were recorded using KRS-5 and germanium reflection elements at 45 and 60° and 45 and 30°, respectively. The depth of penetration into each sample of the reflected ir beam decreases in the sequence KRS-5 45° > KRS-5 60° > Ge 30° > Ge 45°. All observed absorptions are expressed as normalized ratios, relative to the 2840-cm⁻¹ CH absorption of polypropylene.⁶

Luminescence Spectra. Emission spectra were determined on a Farrand Optical Co., Inc., spectrofluorometer (Xe source, 1P-28 photomultiplier). Film samples were firmly gripped in a small "picture frame" mount which slotted diagonally across the standard 1-cm cell holder. The films were mounted at 45° to the excitation beam so that the surface reflected beam could not enter the analyzer. Spectra were recorded in air at 25°; evacuation of the films in quartz cells produced no change in the emission spectra. A rotating chopper attachment in front of the excitation monochromator was used to isolate phosphorescence emission, and a single-pulse shutter was used to determine lifetimes.

Photooxidations. Films were usually irradiated through a Corning CS 1-64 filter (wavelengths >3200 Å) by the Hanovia high-pressure mercury lamp as described previously.²

Some film samples were irradiated under controlled-diffusion conditions with a parallel beam of light from an Osram HBO 500-W super-pressure mercury lamp. This beam was filtered through a Corning CS 1-64 filter and a 10-cm cell of distilled water. Three layers of film were clamped between the halves of a Pyrex 50-mm i.d. O-ring joint so that one side of the film stack was supported on a fine brass mesh. The O-ring joints were fitted with demountable quartz windows at each end, through which the film stack could be irradiated. This cell was arranged so that the film stack was directly irradiated with the supporting mesh behind the samples. Prior to irradiation the cell was continuously evacuated from behind the mesh and air flowed through the front half of the cell. The samples were allowed to equilibrate for 15 hr under these conditions, and then irradiation commenced. After irradiation,

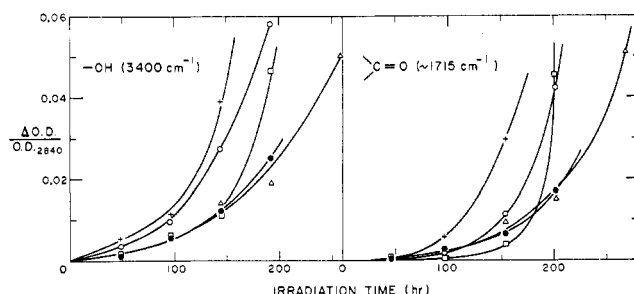


Figure 1. Comparison of the photooxidation of various polypropylene films; irradiation in air at $35 \pm 2^\circ$ with the filtered Hanovia lamp, of films listed in Table I: film A, +; B, ○; C, □; D, Δ; E and F, ●.

the O-ring joint was dismantled and the films were removed and separated for ir analysis. Since both sample temperature and wavelength of irradiation were found to have a marked effect on rate of photooxidation and product distribution, care must be exercised in the comparison of results obtained under differing irradiation conditions.

Corona Treatment. Polypropylene films were exposed to 10 sec of oxygen corona treatment by the previously described procedure.⁸ Oxygen was allowed to flow through the corona cell at atmospheric pressure for 30 min before and after the corona treatment. During the discharge, the gas flow rate was 60 ml min⁻¹. After treatment, the films were turned over, and the reverse side of each film was subjected to an identical 10 sec of corona treatment to ensure similar back and front surfaces. The same procedure was used in the nitrogen corona treatment.

Ozone Treatment. Film samples were exposed to the effluent from an electrolytic ozone generator for 30 sec at room temperature. Exposed films were then immediately evacuated for 10 min.

γ-Initiated Oxidations. Polypropylene films were placed in Pyrex capsules and the capsules evacuated for about 15 hr at 10⁻⁵ Torr. The capsules were then filled with air and sealed off. After 20 hr of storage to allow gas saturation of the films, the capsules were exposed in a Gammabeam 150 (Atomic Energy of Canada Ltd., ⁶⁰Co source) at 27°. Various dose rates were achieved by altering the separation between the capsules and the source.

Results

The relative photostability of polypropylene films prepared from various resins by several manufacturers was compared by the simultaneous irradiation of the films with the filtered light from the Hanovia lamp. The degree of oxidation was measured by following the increase in hydroperoxide (3400 cm⁻¹) and carbonyl (~1715 cm⁻¹) absorptions in the irradiated samples by transmission ir spectroscopy. The reported optical densities (OD) are expressed in terms of the normalized OD values ($\Delta OD/OD_{2840}$) (relative to the 2840-cm⁻¹ polypropylene CH absorption determined during the same scan⁶) to allow comparison with the ATR data and eliminate the effect of sample thickness. These values are shown in Figure 1 as a function of irradiation time. The luminescence spectra of each of these films prior to and during irradiation were also determined. All samples initially displayed the same general emission spectrum with peaks at 3350, 3450, and 3600 Å (weak shoulder), although the total emission intensity varied widely. During irradiation the emission peaks from all samples decreased progressively to virtually zero. An example of the initial emission spectrum and the changes which occur during irradiation are shown in Figure 2 for film D (Table I). Scanning the excitation spectrum of an unirradiated film with the analyzer set to each of the three peak maxima shown in Figure 2 showed that all three emission peaks resulted from absorption maxima at roughly 2350 and 2950 Å (uncorrected for Xe lamp output and photomultiplier response). No emission was detected when the excitation beam was pulsed out of phase with the spectrometer amplifier, whereas similar spectra were recorded when the sample received steady illumination and when it was excited by pulsed illumination which was in phase with the amplifier. The lifetimes of the emitting species were all found to be less than 10⁻⁸ sec with the single pulse shutter. If the lowest emission intensity of the samples examined (film F) is taken as unity, the relative intensities of the 3450-Å band from each polypropylene film (before irradiation) fall in the sequence shown in Table I. All of the above films have been observed to undergo preferential surface oxidation during uv irradiation.²

The possibility of O₂ diffusion control of the photooxidation was investigated by uv irradiating a stack of three films which

TABLE II
 OXIDATION PRODUCT DISTRIBUTION AFTER IRRADIATION^a

Dose rate, Mrad hr ⁻¹	$\Delta OD_{3400}/OD_{2840}$					$\Delta OD_{1715}/OD_{2840}$					% elonga- tion at break
	Trans	KRS-5		Ge		Trans	KRS-5		Ge		
		45°	60°	30°	45°		45°	60°	30°	45°	
0.24 ^b	0.029	0.021	0.024	0.041	0.047	0.020	0.019	0.032	0.041	0.038	0
0.08 ^b	0.015	0.019	0.018	0.021	0.021	0.011	0.020	0.023	0.023	0.024	5
0.03 ^b	0.008	0.012	0.008	0.005	0.002	0.005	0.009	0.008	0.006	0.009	29
<i>c</i>	0.005	0.022	0.028	0.035	0.045	0.004	0.031	0.044	0.074	0.099	12
<i>d</i>	0.013	0.018	0.016	0.019	0.021	0.016	0.024	0.030	0.044	0.051	

^a Irradiation in air; 22- μ film thickness; film A unless otherwise specified. Depth of penetration decreases in the sequence KRS-5 45° > KRS-5 60° > Ge 30° > Ge 45°. ^b γ irradiation at 27° for 40 hr. ^c Uv irradiation for 40 hr, Hanovia lamp, Corning CS 1-64 filter, at 35 \pm 2°. ^d Moplen film prepared under nitrogen, irradiated 84 hr as in footnote c.

was continuously evacuated from one side while the other (irradiated) side was in contact with air at atmospheric pressure. After irradiation for 96 hr, the individual films in the stack were separated, and ATR spectra (at the four different reflection conditions) of the back and front of each film were determined. The variations in normalized ΔOD_{3400} and ΔOD_{1715} values with depth of ir penetration (d_p) into each of these films of the stack are shown in Figure 3, together with the corresponding transmission values. The d_p values employed are those previously cited.⁶

The effects of uv and γ initiation on oxidation were compared when identical 22- μ film samples (film A) were separately oxidized for 40 hr by uv irradiation in air with the filtered Hanovia source, and by γ irradiation at various dose rates in air. The γ dose rates were selected so as to produce total hydroperoxide yields (as measured by transmission ir) similar to those observed in the uv-initiated oxidations. Also other samples containing appreciably greater hydroperoxide yields were produced by γ irradiation. The transmission and ATR ir data for the changes in -OH (3400 cm⁻¹) and >C=O (~1715 cm⁻¹) absorptions of these irradiated samples are shown in Table II. ATR normalized ΔOD values determined for the film surfaces which faced away from the irradiation sources were identical with the corresponding values determined for the surfaces directly facing the sources. Stress-strain curves were also recorded for the 40-hr γ - and uv-irradiated films. Only the percentage elongation at break was found to have been affected by irradiation, and values for this parameter are shown in Table II.

Attempts were made to accentuate the surface oxidation effect by pretreatment of film B. Some samples were subjected to 10 sec of corona treatment on each surface in either

a flowing N₂ or O₂ atmosphere. Other film samples were briefly exposed to the effluent from an ozone generator, and then immediately evacuated to limit the diffusive penetration of O₃ into the samples. These "surface-activated" samples were then uv irradiated under the filtered Hanovia lamp together with samples of film B, and the buildup in oxidation products was followed by ATR and transmission ir spectroscopy. The buildup in hydroperoxide groups for the O₂ corona and untreated samples are compared in Figure 4. The O₃-treated films showed essentially the same product buildup as the O₂-corona-treated films, whereas the N₂-corona-treated samples showed a product buildup identical with that given by the untreated films. An O₂-corona-treated film that was stored in air, but in darkness for the duration of the exposures of the other films, showed no increase in >C=O or -OH ir absorption.

In separate experiments, 30- μ films were prepared by pressing a powdered, unstabilized resin (Moplen) under nitrogen. These films were then irradiated in air with the filtered Hanovia lamp for 84 hr, and the distribution of hydroperoxide and carbonyl groups was determined by ATR and transmission ir spectroscopy (Table II).

Discussion

It is possible to eliminate some of the potential causes of preferential surface photooxidation from a comparison of the distribution of oxidation products produced by the γ and uv irradiation of polypropylene. After irradiation, a uniformly oxidized sample will give ATR normalized ΔOD values for

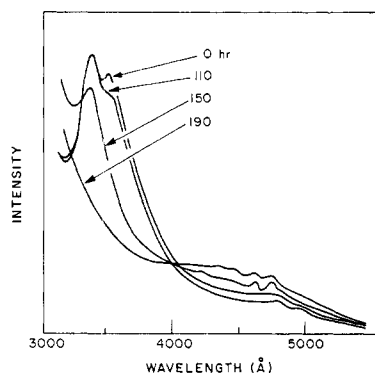


Figure 2. Emission spectrum of a polypropylene film; sample of film D, 2950-Å excitation at 25°; emission intensity, arbitrary units; labels refer to irradiation times (hr) under the conditions described in Figure 1.

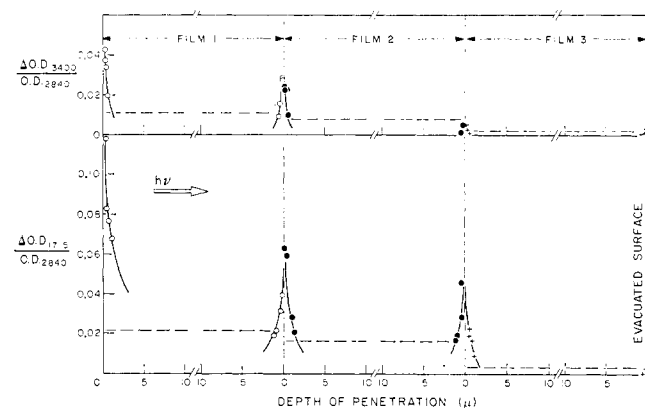


Figure 3. Effect of O₂ diffusion on surface oxidation; three samples of film A, irradiated for 96 hr with the filtered Osram lamp at 30 \pm 2° under controlled air flux; values from transmission spectra, — — —; ATR spectra, —. Depth of penetration measured in from each film surface.

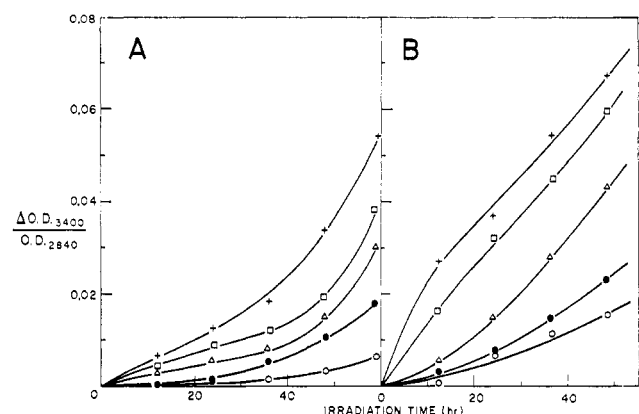


Figure 4. Effects of pretreatment on polypropylene photostability; samples of film B irradiated in air with the filtered Hanovia lamp at $35 \pm 2^\circ$: (A) untreated film, (B) O_2 corona treated film; transmission values, \circ ; ATR values $d_p(\mu) = 0.56$, \bullet ; 0.41 , Δ ; 0.22 , \square ; 0.19 , $+$.

$>C=O$ and $-OH$ which are independent of depth of penetration⁷ of the ir beam, and equal to the corresponding normalized transmission ΔOD values. Preferential surface photooxidation will result in normalized ΔOD values which increase with decreasing depth of penetration.² From Table II, some of the γ -irradiated samples show an increase in $>C=O$ and ROOH concentration with decreasing depth of penetration, but only at relatively high dose rate ($0.24 \text{ Mrad hr}^{-1}$), and hence high rate of oxidation. The γ -irradiated films show ATR normalized ΔOD values which are (within experimental error) independent of d_p at a dose rate of $0.03 \text{ Mrad hr}^{-1}$, and only slightly dependent at $0.08 \text{ Mrad hr}^{-1}$. In addition, the normalized transmission ΔOD values are similar to the observed ATR values. Although there is a complex relationship between $\Delta OD/OD_{2840}$ values and the true concentrations existing at a given depth into the sample,² each normalized ΔOD value is proportional to the concentration at a given depth of penetration and can be used as a convenient measure of extent of oxidation. The γ -irradiation data indicate that uniform oxidation has occurred throughout the polymer during the γ irradiations at the lower dose rates. The photooxidation data for film A (Table II), however, show normalized ΔOD values (both for $>C=O$ and ROOH formation) that increase rapidly with decreasing d_p , even though the total ROOH buildup in 40 hr (as measured by the normalized transmission ΔOD values) is smaller than that observed at either 0.08 or $0.03 \text{ Mrad hr}^{-1}$ dose rate. This increase then indicates extensive photooxidation close to the film surfaces.

The uniform product distribution resulting from γ irradiation at the lower dose rates tends to indicate that the O_2 diffusion into the polymer is sufficiently rapid to replenish O_2 consumed during oxidation. Only at the very high dose rate ($0.24 \text{ Mrad hr}^{-1}$) does O_2 diffusion appear to become limiting, as shown by the slight increase in normalized product ΔOD values with decreasing depth of penetration (Table I). This uniformity of γ -initiated oxidation also precludes the possibilities of enhanced polymer reactivity to O_2 close to the surface. This surface reactivity might have originated from either larger propagation rate constants or lower termination rate constants (relative to the bulk) for the oxidation reactions due to variations in morphology.

(7) The depth of penetration is defined as the distance in which the electric field amplitude falls to a value of $1/e$ of its value at the film-reflection element interface,² and can be thought of as the film thickness which can interact strongly with the reflected ir beam.

The uv- and γ -initiated photooxidations both give hydroperoxide and carbonyl products, although the $[ROOH]/[>C=O]$ ratio from γ irradiation is significantly higher than that observed during uv irradiation. This difference probably results from the ready photolysis of hydroperoxides in the near-uv to give carbonyl products and cause chain scission.⁸ During γ irradiation, carbonyl products are probably only produced by peroxy radical self-termination, or by the unimolecular decomposition of peroxy radicals.⁹ The concurrent formation of the carbonyl products and polypropylene chain scission during photolysis is consistent with the much greater loss in percentage elongation at break during uv irradiation as compared with the loss after γ irradiation at $0.03 \text{ Mrad hr}^{-1}$ (Table II).

Although the γ irradiation results indicate that oxygen diffusion into the polymer is not rate controlling, a more direct experimental proof would be valuable, particularly since oxygen diffusion control has frequently been proposed to occur during the thermal oxidation of polyolefins,¹⁰ and has been predicted theoretically by Wilson.³ With this aim in mind, stacks of three identical films were photooxidized with a fixed O_2 pressure gradient across the films. The ATR normalized ΔOD values for hydroperoxide and carbonyl products formed at various d_p values across each component film are shown in Figure 3 (96-hr irradiation) together with the corresponding transmission values. From Figure 3 it is apparent that preferential oxidation has still occurred close to the surfaces of each of the films comprising the stack. The degree of oxidation at each surface decreases progressively across the stack, owing to the lower O_2 concentration existing at each point.¹¹ The curves shown in Figure 3 then show that the phenomenon of preferential surface oxidation does not result from oxygen depletion caused by the reaction within the film. This conclusion is consistent with a calculated permeability constant for O_2 in polypropylene of $\sim 3 \times 10^{-11} \text{ ml (STP) cm sec}^{-1} \text{ cm}^{-2} \text{ Torr}^{-1}$ at 35° .¹² Although O_2 solubility in polypropylene is low (probably $< 4 \times 10^{-4} \text{ M}$ at 150 Torr of O_2 , from a comparison with published data for argon¹⁴), and the dissolved O_2 will be rapidly depleted during photooxidation (from Figure 1, $> 3 \times 10^{-2} \text{ M}$ ROOH is formed in the first 30 hr of irradiation of film A), even at small pressure differentials diffusion of O_2 into the films is sufficiently rapid (by well over an order of magnitude) to prevent any significant O_2 depletion of a film interior. Depletion might occur after prolonged irradiation when autoacceleration has appreciably increased the photooxidation rate.

The comparison of γ - and uv-initiated oxidation implies that the preferential surface oxidation of uv-irradiated films does not result either from O_2 diffusion limitations or from enhanced polymer surface reactivity to oxygen. Oxidations induced by uv and γ radiation only differ significantly in the initiation step: γ initiation usually occurs uniformly through-

(8) D. J. Carlsson and D. M. Wiles, *Macromolecules*, **2**, 597 (1969).

(9) J. Marchal, Preprints, National Bureau of Standards 4th Materials Research Symposium, Oct 1970, p 77.

(10) See, for example, C. R. Boss and J. C. W. Chien, *J. Polym. Sci., Part A-1*, **4**, 1543 (1966).

(11) Separate experiments in which individual films were irradiated under static conditions in air and O_2 gave ATR and transmission data which indicated that the photooxidation was slightly below half order in oxygen partial pressure.

(12) Estimated from an O_2 permeability constant of $1.5 \times 10^{-11} \text{ ml (STP) cm sec}^{-1} \text{ cm}^{-2} \text{ Torr}^{-1}$ at 25° ,¹³ and an activation energy for permeation of 11 kcal mol^{-1} (as reported for argon diffusion in polypropylene¹⁴).

(13) M. Salame, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **8**, 137 (1967).

(14) W. Vieth and W. F. Wuerth, *J. Appl. Polym. Sci.*, **13**, 685 (1969).

out the sample,⁹ whereas uv initiation is confined to regions containing chromophoric groups. Since "pure" polyolefins are transparent down to $<2000 \text{ \AA}$, photooxidation of polypropylene has been suggested to originate from the absorption of quanta by chromophoric impurities.¹⁵ The rapid surface photooxidation of films then implies a high chromophore concentration close to the surfaces of each film. The photo-initiation of polypropylene degradation has frequently been attributed to the photolysis of either oxidation impurities introduced during processing^{8,16} or residual impurities (e.g., Ti compounds) from the synthesis of the polymer.¹⁷ During processing, even though antioxidants are always present and oxygen is usually excluded from the melt, some thermal oxidation of the resin must occur as the melt is extruded out into the air. This oxidation can be expected to be confined to the surface skin of the extruded polymer since the film is quenched close to the die. For a given resin, the extent of this oxidation will be determined largely by the efficiency of the thermal quenching process employed (water bath, blown air, chill roll, etc.). Hydroperoxides and ketonic products are both produced during the thermal oxidation of polypropylene, and both products have been shown to photolyze in the near-uv to give various radicals which can initiate oxidation.^{8,16} Thus, photoinitiation resulting from the photolysis of chromophores such as these is a potential source of the observed rapid surface photooxidation. This possibility was tested both by attempting to prepare film samples completely free from initial surface impurities, and conversely by attempting to increase the surface concentrations of likely chromophores. Attempts were made to prepare film samples free of surface oxidation products by heating O_2 -free resin under N_2 and squeezing into films under a N_2 atmosphere. The results for the photooxidation of this type of film (Table II) show that hydroperoxide formation has occurred relatively uniformly across the film thickness. Carbonyl products, however, show a small tendency to concentrate toward the film surfaces, although the origin of this effect is not immediately obvious.

Surface concentrations of likely chromophores were generated in samples of film C both by brief O_2 corona treatment and O_3 exposure of samples prior to irradiation. O_2 corona treatment has been shown to be confined to a thin surface skin ($\sim 500 \text{ \AA}$ in thickness), and the observed chemical changes are very similar to O_3 attack on the polymer, although much more controllable than direct O_3 exposure.⁶ Physical modification of the surface (possibly increasing O_2 permeability) by corona treatment appears unlikely since N_2 -corona-treated films showed no enhancement of the surface photooxidation effect as compared to untreated films. When compared with untreated films, both the O_3 - and O_2 -corona-treated films showed a very rapid buildup in hydroperoxide during uv irradiation (Figure 4); carbonyl products showed a similar rapid buildup. O_3 attack on polyolefin unsaturation produces various carbonyl products together with lesser amounts of peroxides and hydroperoxides.¹⁸ Although hydroperoxide or peroxide groups were not detected after O_2 corona or O_3 exposure, small but significant amounts may be formed, together with the carbonyl products previously detected by ATR spectroscopy.⁶ Consequently, the results shown in Figure 4 do not indicate the exact nature of the

chromophore(s) responsible for the accentuated surface photooxidation of the commercial films.

It was hoped that a comparison of the relative uv stabilities of polypropylene films prepared by various manufacturing techniques might yield evidence of surface thermal oxidation during extrusion. This attempt was hindered by the difficulties involved in obtaining polymer films with known histories. From the photooxidation curves shown in Figure 1, it is evident that the films prepared by the chill-roll-quenching method (films A and B) are less stable to uv than the blown films (C, D, and E). This difference between the processes might arise from effects such as differing molecular weights of the starting resins, more rapid quenching of the blown films (films C and D were both manufactured with water cooling), or, alternatively, differing degrees of orientation in the two sets of samples. Chill-roll-quenched films are usually only slightly oriented (in the machine direction), whereas blown films are partially biaxially oriented during the blowing step. The biaxially oriented film F also showed relatively high stability. Orientation might increase stability either by reducing the (photooxidizable) amorphous content (as shown by the high density of film F) or simply by reducing the concentration of surface chromophores per unit area. The uv stability of thin polypropylene film samples has previously been reported to increase with increasing degree of orientation of the film,¹⁹ although the origin of this effect obviously requires further investigation.

The presence of surface carbonyl products in the unirradiated commercial films was evident from their ATR spectra, although only just detectable in most cases. The technique of luminescence spectroscopy provides an alternative, extremely sensitive means of detecting trace impurities. All of the studied samples showed emission similar to that shown in Figure 2. Similar luminescence bands have been reported previously.^{20,21} The three emission bands probably originate from chromophore(s) such as acids or esters (absorbing at $\sim 2350 \text{ \AA}$) and aldehydes or ketones (at $\sim 2950 \text{ \AA}$) and are probably attributable to fluorescence. The relative stabilities of the commercial films shown in Figure 1 are roughly consistent with the relative emission intensities (although the Eastman film is anomalous). However, the steady decrease in all emission intensities during photooxidation (Figure 2) may indicate that the luminescent chromophores do not contribute significantly to the photodegradation, although they may, of course, be very important in the inception of degradation. Alternatively, the decrease in emission might result from the quenching of fluorescent species by other oxidation products. Partridge²⁰ has shown that alkyl ketones cease to emit as the substituent chain length is increased and concluded that the emission from polyolefins is largely due to macroaldehydes rather than ketonic impurities. This conclusion is consistent with the steady decrease in emission from the polypropylene films during photooxidation (Figure 2), despite the large amounts of ketonic oxidation products produced during photooxidation.^{6,8} Consequently, the observed polypropylene emission (Figure 2) can probably be used only as an indication that thermal oxidation has occurred in the polymer films, and not as a true guide to the nature and extent of the oxidation.

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

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

(17) C. Kujirai, S. Hashiya, H. Furuno, and N. Terada, *J. Polym. Sci., Part A-1*, **6**, 589 (1968).

(18) See, for example, J. S. Belew in "Oxidation," Vol. 1, R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1969, pp 259–335.

(19) F. H. McTigue and M. Blumberg, *Appl. Polym. Symp.*, **4**, 175 (1967).

(20) A. Charlesby and R. Partridge, *Proc. Roy. Soc., Ser. A*, **283**, 312 (1965).

(21) A. P. Pivovarov and A. F. Lukovnikov, *Khim. Vys. Energ.*, **2**, 220 (1968).

Conclusions

The proposed importance of traces of oxidation products in the surfaces of freshly extruded films (and of course fibers) leads to several interesting conclusions. Since surface thermal oxidation can be eliminated by N_2 blanketing, this same approach could be applied to commercial extrusion. However, for high-speed extrusions the cost of blanketing is likely to be prohibitive, especially in view of the fact that the gain in uv stability will probably be only two- or threefold. (Presumably other impurities—unsaturation, Ti residues—become the dominant sources of photoinitiation at very low concentrations of oxidation products.) This same degree of stabilization can also be cheaply realized or exceeded by the compounding of an efficient polypropylene uv stabilizer [0.1–0.5 part per hundred resin (phr)] with the resin.

It is now believed that most efficient uv stabilizers operate by accepting energy from uv-excited chromophores in the polymer (and then harmlessly dissipating this energy) rather than solely by a screening mechanism.^{21,22} Such energy-transfer agents must, however, be situated in the immediate vicinity (at least within 50–100 Å) of the excited chromophore for efficient transfer to occur.²³ Since chromophores are

concentrated close to the film surfaces, a large fraction of a uniformly distributed uv stabilizer is ineffective,²⁴ and only additives close to the surface contribute directly to stability. This leads to the possibility of achieving effective uv stabilization by applying a thin surface coating of a stabilizer to a polypropylene film or fiber. Preliminary work indicates that effective stabilization (lifetimes extended *ca.* fivefold) of 22- μ films can be achieved with as little as 0.01 phr of stabilizer which is present as uniform coatings on each surface. This work will be reported in detail in a future publication.

The problem of controlled acceleration of polyolefin degradation during weathering is of current interest in connection with the self-disposal of packaging materials. From Figure 4 it is apparent that a relatively severe pretreatment of polypropylene packaging films by a conventional corona-treatment apparatus (used to improve polymer printability, etc.) might be sufficient to produce a worthwhile acceleration of photodegradation, without sacrificing other essential properties of the films.

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(24) This ineffective stabilizer may play an important secondary role, such as acting as a reservoir of stabilizer for the surface.

Entanglement in Concentrated Solutions of Polystyrene with Narrow Distributions of Molecular Weight

R. I. Wolkowicz and W. C. Forsman*

School of Chemical Engineering and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104. Received April 30, 1970

ABSTRACT: Linear viscoelastic properties were determined for several concentrated solutions of polystyrene with narrow distributions of molecular weight. Measurements were made from the terminal zone to well within the transition zone using a dynamic viscometer of a new design. To interpret the results, we introduced the notion of partial entanglement. For most polymer solutions and melts, a log-log plot of zero-shear-rate viscosity *vs.* molecular weight, M , changes from a straight line segment of slope between 1.0 and 2.0 to one of slope about 3.4 over a relatively narrow range of molecular weights. We defined chain lengths in this molecular weight range as partially entangled; chain lengths below and above this range were considered, in the usual sense, as unentangled and fully entangled. Normal modes of chain motion of index p as defined by Rouse in his theory of viscoelasticity of assemblies of chain molecules correspond to movement of blocks of chain of molecular weights (M/p). This suggests that the various normal modes and their associated relaxation times could also be characterized according to their degrees of entanglement. We then found that Rouse's theory adequately describes the linear viscoelastic behavior of the above polymer solutions when it is modified to include the effects of partial and full entanglement on the longest few relaxation times. Best correlations were obtained by assuming that only odd-order normal modes are affected by entanglement.

Viscoelastic properties of solutions and melts of sufficiently high molecular weight polymers are said to be dominated by the presence of entanglements. The notion that assemblies of long chain-like molecules can form entangled networks has a certain intuitive appeal, especially since it not only explains linear viscoelastic behavior, but non-Newtonian viscosity as well. Nevertheless, it is still true that the concept of chain entanglement has never been placed upon an entirely satisfactory theoretical basis. One of the reasons for this is that there have been few experimental studies of polymer systems with sufficiently narrow distribution of molecular weights. Since most theories have been developed

for monodisperse systems, there has been little opportunity to make critical comparisons between theory and experiment. In this paper we present results from a study of the viscoelastic behavior of concentrated solutions of narrow molecular weight distribution polystyrene and interpret our results in terms of molecular theory proposed by Rouse.¹

We will restrict our deliberations to nonpolar polymer melts and solutions; strong specific intramolecular or intermolecular interactions such as hydrogen bonds could well contribute rheological effects in addition to the entanglement effects of

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