

The Photo-Oxidation of Polypropylene: Some Effects of Molecular Order*

Y. KATO,† D. J. CARLSSON and D. M. WILES, *Division of Applied Chemistry, National Research Council of Canada, Ottawa, Canada*

Synopsis

Fractional crystallization was used to separate a commercial, predominantly isotactic, unstabilized polypropylene into fractions of relatively low and relatively high atacticity, but of similar molecular weight. IR spectroscopy was used to follow the photo-oxidations of films formed from these fractions during irradiation in air with light of wavelengths greater than 3000 Å. The major oxidation products included hydrogen-bonded hydroperoxides and carbonyl compounds. Films of constant tacticity, but varying morphology were prepared by quenching from the melt. No distinct correlation was found between sample photostability and morphology, as indicated by film density. Films of low atactic content were found to undergo faster photo-oxidation than films of high atactic content, irradiated under identical conditions. This effect is believed to be due to the occurrence of a stereo-dependent step (or steps) in the oxidative chain, and not due to differences in sample morphology. The possible nature of the stereo-dependent steps is considered in terms of well-established oxidative chain processes. The effects of polypropylene polymorphism on oxygen permeability are briefly considered.

INTRODUCTION

Although the thermal oxidation of polypropylene has been investigated in both the solid¹ and liquid phases,² comparatively little work has been published on the factors influencing the photo-oxidation of the polymer.^{3,4} Variations in polyethylene morphology^{5,6} and polypropylene stereoregularity² have been reported as having a marked effect on the oxidative stability of these polymers. This paper describes an investigation of the role of polymer tacticity on the photo-oxidation of polypropylene films, together with the associated role of polymer morphology. Irradiation conditions were chosen to approximate outdoor exposure, i.e., ambient temperature, and wavelengths greater than 3000 Å.

* N.R.C.C. No. 10912.

† N.R.C.C. Postdoctoral Fellow 1967-1968; present address: Electrical Communication Laboratory, Nippon Telegraph & Telephone Public Corporation, Tokai, Ibaraki, Japan.

EXPERIMENTAL

Polymer crystallization

Samples of varying atactic content were prepared by the fractional crystallization of an unstabilized, commercial-grade of Hercules polypropylene (designated CV 159-62, M.Wt. = 3.7×10^5).

To prevent the thermal oxidation of the unstabilized polymer, the fractional crystallization apparatus,⁷ was modified so that the polymer solution could be saturated with nitrogen throughout the separation.⁸ Polymer samples were dissolved in xylene at 135° to give concentrations of about 10 g/l, and then each solution was allowed to crystallize at the required temperature, determined by a vapor bath. Crystallization times were varied from 2 to 40 hr at a specific temperature and the crystallization temperatures for different separations ranged from 23° to 80°. After crystallization, the xylene solution containing the uncrystallized portion (L fraction) was siphoned through a glass filter and precipitated in methanol. The crystallized portion (H fraction) was redissolved in hot xylene and precipitated in methanol. Both fractions were vacuum dried at room temperature.

Intrinsic viscosities were determined from measurements made in decalin at 135°. Molecular weights were calculated from the expression of Kinsinger and Hughes.⁹

Film preparation

Polypropylene films of uniform thickness (about 80 μ) were prepared by squeezing polymer samples in a nitrogen atmosphere between Teflon sheets at 200 p.s.i. The press temperatures were 200° and 140° for the H and L fractions respectively. The molded films were transferred to a vacuum press (5×10^{-4} mm Hg) and briefly squeezed (about 2 p.s.i.) between thin aluminum foils at 200° (H fraction) or 160° (L fraction) to give films with smooth surfaces. These foil-film sandwiches were then removed from the press and immediately quenched to particular temperatures, to give the desired film density.

Film density values were used as a comparative indication of morphological differences,^{10,11,12} and were measured by flotation in water/methanol mixtures. The morphologies of the film samples were also compared by optical microscopy, under crossed Polaroids.

Each film was characterized by infrared (IR) spectroscopy using a Beckman IR8 with a scale expansion unit. The atactic content of each sample was estimated from the ratio of the 974 cm^{-1} band to the 995 cm^{-1} band.¹³ This technique gives a convenient estimate of relative tacticities, although the absolute significance of such values has been questioned.¹⁴

Photo-oxidation

Film samples were irradiated with a Hanovia, high-pressure, quartz, mercury-vapor lamp (450 watt, L-burner) through a Corning filter (C. S.

0-53, 2 mm, transmission $\geq 25\%$ at wavelength $\geq 3000 \text{ \AA}$). The lamp-sample distance was 26.5 cm, and the sample temperature $33 \pm 2^\circ$. The build up of photooxidation products in each film was followed by changes in IR absorption.

Preliminary experiments showed a marked dependence of the rate of photo-oxidation on source intensity. To eliminate this effect, samples of, for example, differing density were either irradiated simultaneously, or under identical irradiation conditions. Samples of differing tacticity were treated similarly. Photo-oxidation rates showed a marked dependence on oxygen partial pressure. All of the results reported in this paper were obtained by irradiation in air.

Volatile organics produced during photo-oxidation were collected by oxidizing a film sample in a sealed system, and then pumping the residual air and volatile products through a trap cooled in liquid nitrogen. The condensed volatiles were analyzed by gas chromatography, using a Porapak 'R' column (Waters Associates Inc.).

RESULTS

Fractional crystallization

The fractionation technique of Kamath and Wild was employed since the procedure gives reproducible separations, with respect to stereoregularity, and the separation is not influenced by molecular weight.⁷ The variation of the atactic content of H and L fractions as a function of crystallization conditions is shown in Table I. By varying the crystallization conditions, it was found that fractions of reproducible atactic content were obtained after 20 hr at a concentration of 1 g/100 ml even at 65° . The atactic con-

TABLE I
Fractional Crystallization of Polypropylene

Crystallization		Polymer solution conc. (g/100 ml)	Fraction		Atactic content L-fraction, %
Temp., $^\circ\text{C}$	Period, hr		L, wt. %	H, wt.% ^b	
80	22.0	1.0	87	13	30
69	23.0	1.0	— ^a	— ^a	52
65	4.0	1.0	— ^a	— ^a	50
65	20.0	1.0	14 ^c	86 ^d	56
65	22.0	0.25	28	72	58
56	2.5	1.0	12	88	51
56	20.0	1.0	10 ^e	90	63
23	23.5	1.0	3	97	88
23	26.0	2.0	3	97	86

^a Not determined.

^b Atactic content 20-25%.

^c M. Wt. = 1.44×10^5 .

^d M. Wt. = 4.36×10^5 .

^e M. Wt. = 1.41×10^5 .

tent of each H fraction was estimated by IR spectroscopy to be between 20 and 25 percent.

It is convenient to define each fraction prepared by the letter H (crystalline fraction) or L (solution fraction) followed by two suffixes, the first indicating the crystallization temperature, and the second the film quenching temperature (N denotes quenching in liquid nitrogen).

As shown in Table I, the change of molecular weight caused by fractional crystallization was not significant. All fractions except L-23 had molecular weights of the same order. All film samples were initially free of —OH or carbonyl, IR absorption (O. D. < 0.003) indicating the absence of significant thermal oxidation during fractionation or processing.

Photo-oxidation of Polypropylene

The photo-oxidation of polypropylene causes marked changes in the IR spectra of the polymer films at about 3400 cm^{-1} (—OH region) and about 1720 cm^{-1} (carbonyl region) as shown in Figure 1. Irradiation wavelength was found to have a profound effect on the rate of photo-oxidation and also on the relative proportions of the products.¹⁵ Consequently, in this paper all photo-oxidations involve irradiation with a single spectral distribution (3000 \AA and greater).

By analogy with the thermal oxidation of polypropylene,¹¹ it was concluded that the 3340 cm^{-1} band is caused by hydrogen-bonded hydroperoxides produced by the oxidation of tertiary C—H bonds. Free —OH was not detected in any photo-oxidized samples. The presence of hydroperoxide was confirmed by chemical analysis. Quantitative determination of hydroperoxide and of residual —OH after complete decomposition of the hydroperoxides indicated the presence of some alcohol, which contributed up to 10% of the 3340 cm^{-1} band.

The carbonyl oxidation products produce a broad absorption extending from 1650 to 1850 cm^{-1} , which consists of several bands. However, the band shape at constant wavelength of irradiation was found to be indepen-

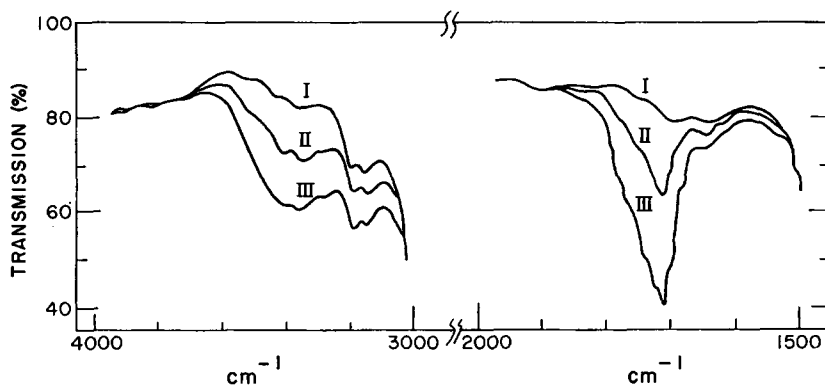


Fig. 1. Photo-oxidation products of H-23-100 film. —OH and C=O build up in air. (I) 0 hr; (II) 65 hr; and (III) 110 hr.

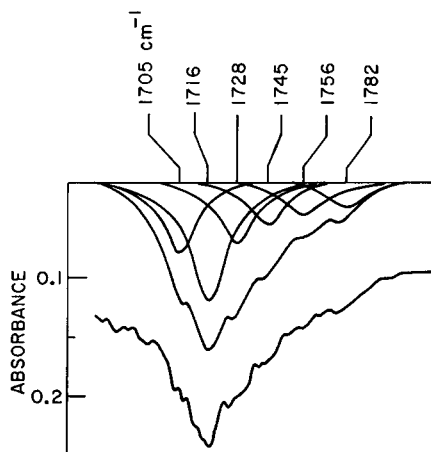


Fig. 2. Photo-oxidation products. Composition of the carbonyl absorption.

dent of the degree of oxidation. The band can be separated into six overlapping absorptions which together reproduce the whole contour of the carbonyl absorption as shown in Figure 2. A Lorentzian line shape with a width at half height of 20 cm^{-1} has been assumed for each absorption. Assignment of these absorptions is based on literature values.^{17,18,19} Also, using the literature values of extinction coefficients of carbonyl absorptions,¹⁹ the total concentration of carbonyl products was always calculated to be proportional to about three times the ketone absorption at 1716 cm^{-1} . Since the extinction coefficient for hydrogen-bonded hydroperoxide absorption at 3340 cm^{-1} is about $70\text{ M}^{-1}\text{ cm}^{-1}$ (calculated from the chemically determined total peroxide content of several films) and for ketones the extinction at 1716 cm^{-1} is about $220\text{ M}^{-1}\text{ cm}^{-1}$, the ratio of absorptions ($D_{1716\text{ cm}^{-1}}/D_{3340\text{ cm}^{-1}}$) is a direct measure of the relative concentrations of carbonyl products and hydroperoxides in the film sample.

Sample thickness is known to affect the rate of oxidation of polyolefin films.¹ To avoid this variation, all prepared films were of $80\text{ }\mu$ thickness.

Effect of morphology on photo-oxidation

A decrease in the atactic content of a stereoregular polymer will automatically cause an increase in the amount of available, crystallizable polymer. Conflicting reports of the effect of polymer crystallinity on gas permeability have been published.^{12,20} Thus the effect of tacticity on the photo-oxidation of polypropylene cannot be studied without a prior knowledge of the effect of morphology on the oxidation under our experimental conditions. Owing to the polymorphism of polypropylene, the preparation of samples of reproducible morphology requires the strict control of film thickness, nature of the substrate and quenching conditions.²¹ Several samples of varying morphology were prepared by quenching films of con-

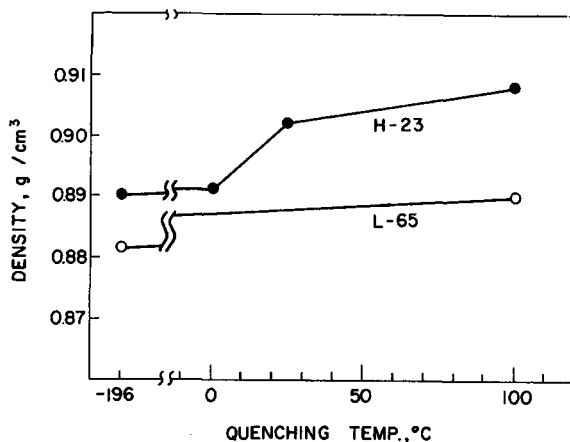


Fig. 3. Effect of quenching temperature on film density.

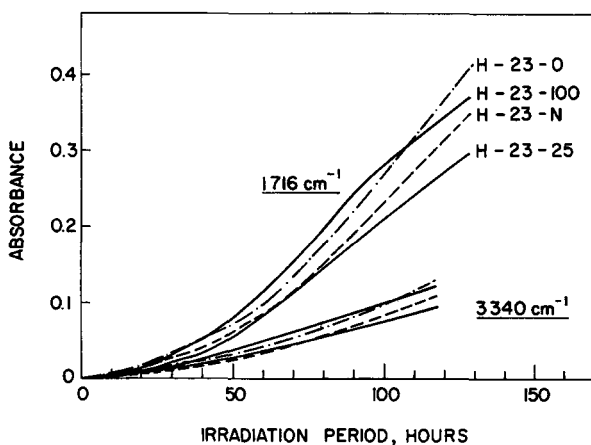


Fig. 4. Effect of morphology on photo-oxidation.

stant atactic content (H-23) at varying temperatures. The effect of quenching temperature on density is shown in Figure 3. Optical microscopy showed that all of the quenched H films (including those quenched at 100°) contained only small, needle-like birefringent crystallites (less than 1 μ in length), rather than spherulitic aggregates.

Figure 4 shows an example of the build-up in oxidation products during the simultaneous irradiation of four H-23 films with the filtered Hanovia source. During repeat experiments, the relative positions of these product curves were found to scatter about the mean value of the curves shown in Figure 4. Figure 5 shows a typical effect of film quenching temperature on the ratios of carbonyl products to hydroperoxide at several irradiation times. After an initial scatter (prior to the acceleration of the oxidation curves in Fig. 4) the product ratios were quite reproducible and showed

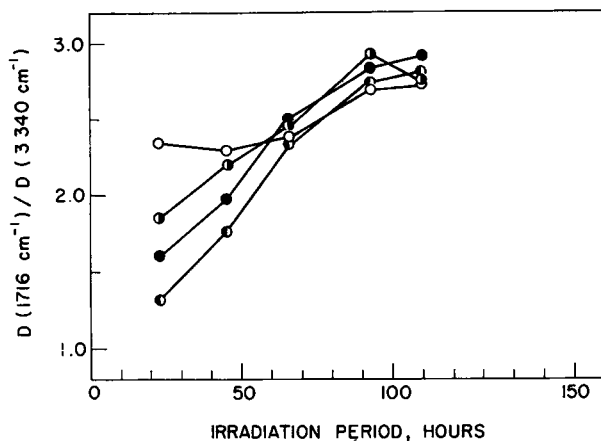


Fig. 5. Effect of morphology on photo-oxidation.

similar values at a given irradiation period for samples quenched under widely differing conditions. The early stages of each photo-oxidation are undoubtedly complicated by the presence of trace impurities,²² and in addition there is a large experimental error involved in the measurement of these very low product concentrations.

The press temperature used in the film preparation was found to have no effect on the photostability of the samples. The results shown in Figure 4 must be affected to some extent by variations in transparency associated with samples of differing crystallinity, although the product ratios in Figure 5 will be independent of these transparency variations. The variation of percentage transmission at 3500 Å with quenching temperature was found to be 83% (−196°), 85% (0°), 73% (25°) and 73% (100°). Correction for this variation in transmission (±6%) will not, however, appreciably change the oxidation curves in Figure 4. From Figures 4 and 5 it seems reasonable to conclude that morphological variations at constant tacticity have relatively little effect on the rate of formation of photo-oxidation products. It is assumed that, under our experimental conditions, morphological variations at different tacticities will also have little influence on the photo-oxidation.

Effect of tacticity on photo-oxidation

As indicated in Figure 3, it is possible to produce samples of very similar density but differing tacticities by quenching L fractions at 100° and H fractions at −196°. This technique was frequently employed to minimize the possibility of interfering morphological effects. Transparency of L fractions varied little with quenching temperature (76% at −196° and 72% at 100°). Films formed from H fractions and carefully annealed all showed densely packed spherulites under low magnification. Annealed films of L fractions, however, showed only isolated spherulites interspersed with birefringent crystallites, indicating some crystallizable material in a pre-

dominantly uncrystallizable matrix. Quenched films of L fractions showed no detectable crystallites (up to $\times 120$ magnification).

Film samples of varying atactic content were photo-oxidized with the light from the filtered Hanovia lamp. Pairs of films prepared from the H and L portions of a fractional crystallization were irradiated simultaneously,

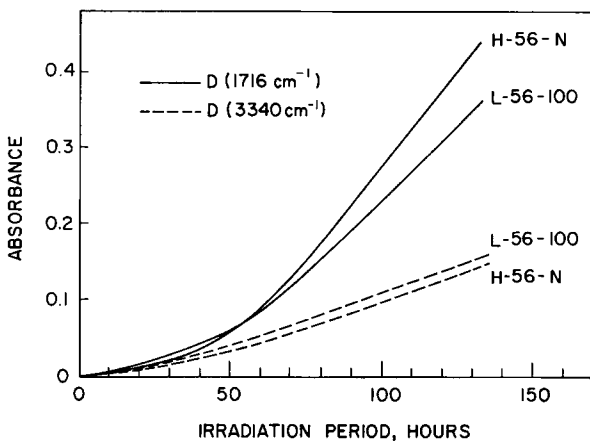


Fig. 6. Effect of tacticity on photo-oxidation.

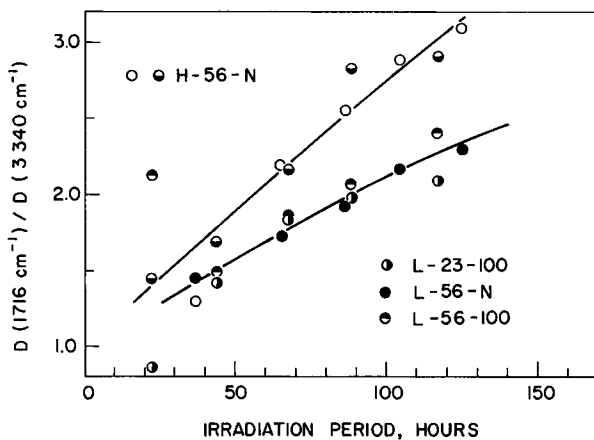


Fig. 7. Effect of tacticity on photo-oxidation.

and the average build up in oxidation products obtained from several pairs of films is shown in Figure 6. A small, though significant difference in the rate of formation of carbonyl products in the two fractions was found. This effect is more clearly shown by the variation in the absorption ratio in Figure 7. The more rapid increase in the absorption ratio of H fractions as

compared to L fractions was also found with samples prepared under different quenching conditions, or at different fractional crystallization temperatures. Scatter in the early stages of photo-oxidation is again attributed to

TABLE II
Photo-oxidation Products*

Component	H-fraction	L-fraction
	(Mole %)	(Mole %)
C ₂ hydrocarbons	12	11
C ₃ "	12	8
C ₄ "	7	6
C ₅ "	—	1
CH ₃ CHO	13	15
CH ₃ COCH ₃	41	48
(CH ₃) ₂ CHOH	—	4
(CH ₃) ₂ CHCHO	1	1
CH ₃ COC ₂ H ₅	1	3
CH ₃ COOH	13	3
Total organics (μ mole)	1.2	0.5

* H- and L-films irradiated under identical conditions.

impurity effects and low product levels. Both H and L film samples gave identical carbonyl band shapes on photo-oxidation.

The difference in oxidative behavior of the H and L fractions is even more apparent when account is taken of the loss of low molecular weight organic products from the film samples during oxidation. G. 1. c. analysis shows that these products are mainly acetone, acetaldehyde and some hydrocarbons as shown in Table II. The amount of volatile carbonyl products from an H or L film during 50 hr photo-oxidation is about five times the residual concentration detected by the IR absorption of each film. The volatile carbonyl products are probably formed by the secondary photolysis of high molecular weight carbonyl compounds.²² However, the residual carbonyl concentration is still directly related to the extent of oxidation of each sample since an H fraction yields significantly more volatiles than an L fraction under identical irradiation conditions.

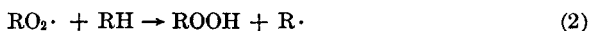
DISCUSSION

Figure 6 indicates that high isotacticity apparently results in a more rapid photo-oxidative attack on polypropylene film samples, as compared with the more atactic samples studied. It is possible that this difference may be attributable to effects other than stereoregularity. For example, differences in molecular weight or molecular weight distribution will introduce the possibility of different numbers of end groups in each fraction. However, the molecular weights of the fractions separated by crystallization at 65° were found to differ only slightly (Table I). IR spectroscopy

showed a small increase in degree of C—C unsaturation (vinyl and vinylidene) with increasing atactic content. Unsaturation may influence photo-oxidation in the very early stages (30 ~ 50 hr of filtered Hanovia irradiation) but should be unimportant after the build up of oxidation products which can undergo rapid photolysis.²² Large percentages of unsaturation have been shown to have little effect on the thermal oxidation of polyethylene.²³

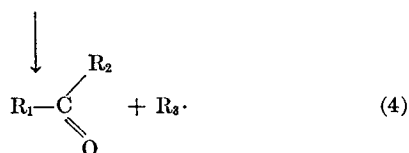
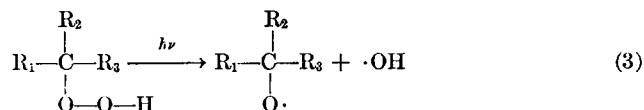
Fractional crystallization of polypropylene may result in the concentration of impurities in the solution (L) fraction. The most atactic fraction (L-23) obtained by crystallization was not frequently used in the photo-oxidations partly because of the low yield of this fraction, but mainly because of the possibility of a high impurity level. However, impurity concentration in the 56° fractions was shown to be unimportant when an H-23 fraction was recrystallized into H- and L-fractions at 56°. No essential difference was found when the photo-oxidation of films formed from the above refractionated fractions was compared with H-56 and L-56 films formed by direct fractionation.

The photo-oxidation of polypropylene (RH) is believed to propagate by a radical chain mechanism [eq. (1) and (2)] similar to the thermal oxidation of the polymer.^{1,2}



The differing photo-oxidative behaviour of atactic and isotactic polypropylene samples is probably caused by some conformational dependence of the oxidation mechanism. The experimental results in Figure 6 show that the rates of hydroperoxide build-up in an isotactic and an atactic sample are very similar. However, the overall rate of oxidation (given by the total concentration of oxidation products) and the rate of carbonyl formation relative to hydroperoxide formation are markedly greater in the more isotactic sample (H-56). As carbonyl products mainly arise from the decomposition of hydroperoxides, hydroperoxide formation and decomposition must occur more rapidly in the sample of greater stereoregularity. These differences in oxidation behaviour may arise in any of the oxidation steps, i.e., initiation, propagation or termination.

The faster thermal oxidation of isotactic polypropylene in solution at 120–140° as compared with the atactic or syndiotactic polymer has been attributed to an intramolecular attack of a t-RO₂· [eq. (2)] on a neighbouring t—C—H group.² However, solution-oxidized syndiotactic polypropylene has been shown to contain hydrogen-bonded hydroperoxide sequences¹⁶ similar to those proposed for the isotactic polymers. It seems likely that all conformations of polypropylene can undergo intramolecular attack, although stereoregularity may still influence the rate of reaction 2. Hydroperoxide photolysis to radicals occurs rapidly, even at wavelengths greater than 3000 Å (reaction 3).²⁴



These radicals may initiate oxidation by hydrogen abstraction, or the alkoxy radical may undergo β -scission to give carbonyl products (eq. 4).²⁵ The experimentally observed, greater rate of hydroperoxide photolysis in the isotactic fraction may arise from a higher quantum yield for photolysis. However, the primary quantum yield should be about 1.0 even in the atactic polymer.²⁴ Alternatively, radical-induced decomposition of adjacent hydroperoxide groups could occur after the initial photolysis of one hydroperoxide. Induced decomposition will certainly be more extensive in regions of high hydroperoxide concentration, which result from neighbouring t-C-H attack. Radical chain termination will depend to some extent on the mobility of the polymer chains. If mobility is higher in the more random, atactic samples than in the more ordered, isotactic films, this could lead to a more frequent association between R·, RO· and RO₂· in the atactic polymer, and a consequent greater rate of chain termination than in the isotactic polymer.*

On the basis of the above discussion, it is impossible to make a positive selection of the critical, stereo-dependent step(s). An interplay of several factors is probably required to explain the experimental data.

The oxidation of polymer films obviously requires access of molecular oxygen to the polymer chains. The relationship between oxygen permeability and the morphology of polypropylene samples crystallized from the melt is complicated by the coexistence of three phases (amorphous, smectic and crystalline). The solubility data of Michaels and Bixler²⁷ for polyethylene show that crystalline regions are impermeable, and amorphous regions permeable to most gases, although the amorphous permeability has been shown to be dependent on the size, shape and size distribution of crystallinities.²⁰ This general picture probably can be applied to oxygen diffusion in polypropylene as the smectic and crystalline states can be expected to have similar permeabilities.

The experimentally observed increase in density at constant tacticity (Fig. 3) suggests an increase in the total degree of order, presumably by an increase in monoclinic crystallinity at the expense of smectic order, combined with an increase in crystallite size.²⁸ The lack of correlation between quenching temperature (i.e., initial density) and the rate of film photo-oxidation (an oxygen-pressure dependent and hence diffusion-controlled

* From a comparison with the liquid phase reactions of t-peroxy radicals,²⁶ combination can be nonterminating. However, even in the atactic samples it is unlikely that there will be sufficient molecular mobility to prevent the termination.

process), may indicate that there is little change in overall permeability with increasing density (cf. reference 20). Alternative explanations for this absence may involve chemicrystallization,^{4,5,6} annealing at the irradiation temperature,²⁹ specific surface effects, or compensating effects involving oxygen permeability and radical termination. A complex dependence of photostability of polypropylene³ and polyethylene⁴ on polymer density and crystallinity has already been reported. Comparison of our experimental results with those obtained by the Fade-Ometer photo-oxidation of stabilized polypropylene³ is not possible, due to the wide differences in the nature of the film samples, and in the irradiation conditions.

Rationalization of the physical processes involved in the photo-oxidation of polyolefins will require a detailed study of the oxygen permeability, oxygen solubility and x-ray crystallinity for samples of controlled morphology.

References

1. C. R. Boss and J. C. W. Chien, *J. Polym. Sci.*, **A1** **4**, 1543 (1966).
2. L. Dulog, E. Radlmann, and W. Kern, *Makromol. Chem.*, **60**, 1 (1963); *ibid.*, **80**, 67 (1964).
3. F. H. McTigue and M. Blumberg, *Appl. Polym. Symposium*, **4**, 175 (1967).
4. R. Vesely, *J. Polym. Sci.*, **C** **16**, 405 (1967).
5. F. H. Winslow, W. Matreyek, and S. M. Stills, *A.C.S. Polym.* preprints, **7**, 390 (Jan. 1966).
6. F. H. Winslow, M. Y. Hellman, W. Matreyek, and S. M. Stills, *Polym. Eng. Sci.*, **6**, 273 (1966).
7. P. M. Kamath and L. Wild, *Polym. Eng. Sci.*, **6**, 213 (1966).
8. C. A. Russell, *J. Appl. Polym. Sci.*, **4**, 219 (1960).
9. J. B. Kinsinger and R. E. Hughes, *J. Phys. Chem.*, **63**, 2002 (1959).
10. R. G. Quynn, J. L. Riley, D. A. Young, and H. D. Noether, *J. Appl. Polym. Sci.*, **2**, 166 (1959).
11. G. W. Schael, *J. Appl. Polym. Sci.*, **10**, 901 (1966).
12. W. P. Conner and G. L. Schertz, *S.P.E. Trans.*, **3**, 186 (1963).
13. J. P. Luongo, *J. Appl. Polym. Sci.*, **3**, 302 (1960).
14. J. P. Sibilia and R. C. Winckhofer, *J. Appl. Polym. Sci.*, **6**, S56 (1962).
15. Y. Kato, D. J. Carlsson, and D. M. Wiles, unpublished results.
16. J. C. W. Chien, E. J. Vandenberg, and H. Jabloner, *J. Polym. Sci.*, **A1** **6**, 387 (1968).
17. F. M. Rugg, J. J. Smith, and R. C. Bacon, *J. Polym. Sci.*, **13**, 535 (1954).
18. J. P. Luongo, *J. Polym. Sci.*, **42**, 139 (1960).
19. J. F. Heacock, *J. Appl. Polym. Sci.*, **7**, 2319 (1963).
20. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 413 (1961).
21. D. M. Gezovich and P. H. Geil, *Polym. Eng. Sci.*, **8**, 202 (1968).
22. D. J. Carlsson, Y. Kato, and D. M. Wiles, *Makromol.* **1**, 459 (1968).
23. T. H. Meltzer, J. J. Kelley, and R. N. Goldey, *J. Appl. Polym. Sci.*, **3**, 84 (1960).
24. J. T. Martin and R. G. W. Norrish, *Proc. Royal Soc. (London)*, **A220**, 322 (1953).
25. J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, **30**, 3272 (1965).
26. J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **46**, 2655 (1968).
27. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 393 (1961).
28. J. J. P. B. Blais and R. St. John Manley, *J. Makromol. Sci.*, **B1**, 525 (1967).
29. G. Farrow, *J. Appl. Polym. Sci.*, **9**, 1227 (1965).

Received December 11, 1968

Revised February 5, 1969