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Publisher's version / Version de l'éditeur:
https://doi.org/10.1016/0141-3910(87)90054-1
Polymer Degradation and Stability, 19, 3, pp. 195-206, 1987

Polymer Degradation and Stability **19** (1987) 195–206

Oxidation of Solid Polyethylene Films: Effects of Backbone Branching*

D. J. Carlsson, G. Bazan, S. Chmela, D. M. Wiles

Division of Chemistry, National Research Council of Canada, Ottawa, Canada, K1A OR9

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K. E. Russell

Department of Chemistry, Queen's University, Kingston, Canada, K7L 3N6

(Received 20 April 1987; accepted 22 April 1987)

ABSTRACT

The oxidation rates and product distribution of a series of linear and branched polyethylene films have been studied when initiated by γ-irradiation. Branch groups in laboratory-synthesized samples ranged from ethyl to $C_{16}H_{33}$*—and were at levels comparable with those found in commercial linear-low and low-density polyethylenes. In the complete absence of stabilizers and at the controlled rates of radical formation possible with γ-irradiation, all of the polyethylene samples oxidized at essentially the same rate to give the same mixture and distribution of products. The differences in oxidation rates previously attributed to the presence of tert. C—H groups at branch sites more probably originate from the effects of impurities, especially on photo- and thermal initiation processes.*

INTRODUCTION

Although the oxidative degradation of polyethylene has been extensively studied over the last 40 years, a surprisingly large number of questions

* Issued as NRCC No. 28125.

Polymer Degradation and Stability 0141-3910/87/$03·50

remain unanswered. The most important questions concern the rate of oxidation of the various polyethylenes commercially available and the relationship between the chemical oxidation process and the dramatic loss of physical properties. In this paper, we are concerned with the effect of chain branching on the true rate of polyethylene oxidation. 'True' rate in this context means the intrinsic rate of oxidation for a constant rate of initiation. Several studies have resulted in the conclusion that branched polyethylenes oxidize more rapidly than their linear analogues because of the presence of the tert. C—H site at each branch point.[1-5] However, these studies have often been on poorly characterized polymers, and have depended upon data from photo- and thermally initiated oxidations. In each case, the initiation of oxidation by these two processes is completely dependent on the presence of adventitious impurities and on the stability of the molecular oxidation products (especially hydroperoxide groups) under the oxidation conditions. More recently, some evidence for the absence of a branching effect on oxidation has appeared, although in many cases for ill characterized samples or oxidation products.[6-9]

The use of γ-irradiation provides an alternative, highly controllable mechanism for initiating oxidations at close to ambient temperature. We have examined the γ-initiated oxidation of a series of polyethylene resins, both industrial and laboratory products, chosen to contain a variety in branch types and branch frequencies.

EXPERIMENTAL

A series of random, C_2H_4/alkene-1 copolymers was prepared by the use of an aluminum sesquichloride–vanadium oxychloride catalyst system.[10] These polymers were hot pressed between chromed plates into films under a nitrogen atmosphere and quenched in cold water. Commercial films examined included a high pressure polymerized film (LDPE, 33 μm, Union Carbide), a low pressure polymerized film containing an alkene-1 comonomer (LLDPE, 105 μm DuPont Canada, Sclair) and a high density film (HDPE 28 μm, Union Carbide). For comparison purposes, a commercial isotactic polypropylene (PP) film (25 μm, Himont Profax, blown film) was also examined, together with a film pressed from poly(butene-1) homopolymer (Shell) and from an extremely linear, ultra high molecular weight polyethylene (Himont UHMW 1900). All films were Soxhlet extracted for 48 h with acetone to remove any antioxidants and then vacuum dried.

Film analyses before and after oxidation were made by Fourier Transform infra-red (FTIR) spectroscopy (Perkin-Elmer 1500, TGS

detector, 200 scans). FTIR spectra were recorded with an efficient wire-grid polariser set at 0° and the samples tilted at the Brewster angle so as to eliminate interference ripples and allow the detection of small oxidation bands.[11] Prior to oxidation, films were further characterized by differential scanning calorimetry (DSC, DuPont 1090) and density measurement (flotation in hexane–chloroform mixtures). The branch contents of the laboratory-synthesized copolymers were determined by ^{13}C nmr.[10]

The polyethylenes were oxidized in air in a Gamma Cell 200 [Atomic Energy of Canada, dose rate 1·0 Mrad h^{-1} (10 KGy h^{-1}), sample chamber temperature 40°C during irradiation]. FTIR spectra were recorded before and immediately after irradiation. A few film samples were also photo-oxidized in a xenon arc WeatherOmeter (Atlas, 2500 W) for comparison purposes.

In order to further characterize and quantify the oxidation products, samples of the oxidized films were exposed for 15 h to gaseous NO or to SF_4, respectively. FTIR spectra were recorded after exposure to these reactive gases as described previously.[12,13] Total hydroperoxide yields were estimated by iodometry.[14]

The yields of radicals produced by γ-irradiation of the polyolefin films were determined in separate oxidation experiments in which the samples were γ-irradiated in air at low temperature and transferred cold to fresh esr tubes. Radicals were observed by electron spin resonance (esr) spectroscopy (Varian E4 equipped with a variable temperature cavity) and quantified by computerized double integration [Apple II+ using an Adalab analogue to digital converter and Vidichart (Interactive Microwave Inc.) software]. Diphenylpicrylhydrazyl in benzene was used to calibrate the esr spectrometer for concentration measurements.

RESULTS

The type of branching in PE samples can be established and quantified conveniently by ir spectroscopy.[1,15–17] Hexadecane was used to determine the ir extinction coefficient (ε) for the deformation of CH_3-groups on branches other than ethyl side groups ($\varepsilon = 14{\cdot}1$ liter $mole^{-1}$ cm^{-1} for the 1378 cm^{-1} absorption). CH_3-deformation vibrations in ethyl side groups are well known to have a higher value, and this was estimated from the spectra of poly(butene-1) film ($\varepsilon = 17{\cdot}1$ liter $mole^{-1}$ cm^{-1} for the 1379 cm^{-1} absorption). Ethyl branches were identified and also quantified by their weak 780 cm^{-1} absorption ($\varepsilon = 4{\cdot}5$ liter $mole^{-1}$ cm^{-1}). The 923 cm^{-1} absorption shown by poly(butene-1) is not found in random butene-1/ethylene copolymers and is indicative of butene-1 blocks.[1,15] Because of

overlap of the 1378–1379 cm^{-1} CH_3-absorption with the 1368 cm^{-1} absorption from amorphous —CH_2-groups, the spectrum of the UHMWPE film was subtracted from the spectrum of each laboratory-synthesized and commercial PE studied as proposed by McRae & Maddams.[15] The subtraction was scaled on the FTIR computer to completely suppress the 1368 cm^{-1} absorption so that the 1378–1379 cm^{-1} absorption could be more accurately measured. This rapid procedure is equivalent to the laborious wedge compensation method proposed by ASTM.[16]

Total branching (expressed as tert. C—H sites) and ethyl branching for the various films oxidized are listed in Table 1. Only the LDPE and LLDPE samples were found to contain ethyl branches, as did the butene-1 copolymer, of course. Vinyl end group levels were estimated from the 910 cm^{-1} absorption ($\varepsilon = 121$ liter $mole^{-1}$ cm^{-1}).[18] Although vinylidene groups absorb at 888 cm^{-1}, their quantification in branched LDPE samples (branches $\geq C_3H_7$—) is complicated by overlap with the 888 cm^{-1} side chain absorption.[9,17]

DSC curves for the laboratory copolymers and the commercial LDPE film were typical of branched polyethylenes, with extensive pre-melting which began at 40–60°C below the sharp melting endotherm. Only first-melting behaviour is reported, as indicative of the morphology in each film. The quoted heats of fusion (Table 1) refer to the total melting process. HDPE and PP films gave simple DSC curves with very sharp single endotherms, whereas the LLDPE was much more complex. The DSC curve for this latter sample indicates the presence of branched PE and linear PE, in the proportion of 33:1 based on the observed component heats of fusion. 'Crystallinity' values may be estimated from the total observed heat of fusion and assumed values of 280 J g^{-1} and 209 J g^{-1} for the heats of fusion of perfectly crystalline PE and PP, respectively.[19] Alternatively, 'crystallinity' values may be derived from the density measurements (density = 1·014 and 0·854 g cm^{-3} for perfectly crystalline and amorphous PE, respectively).[20]

The γ-irradiation of polymers produces free radicals as end products from a complex, extremely rapid sequence of events, involving highly excited states, ions and electrons.[21] Our esr data showed that very similar total yields of radicals were produced upon γ-irradiation of each film either at 77 K in air or vacuum or at −78°C in air. The types and proportion of radicals were, however, different. Under vacuum irradiation, only macro-alkyl radicals were observed, whereas irradiation with air present at 77 K produces a mix of macro alkyl and peroxyl radicals. By irradiation at −78°C in air, or upon warming to −78°C in the presence of air after irradiation at 77 K, the macro alkyl radicals convert virtually completely to peroxyl

TABLE 1
Polyolefin Film Properties

Sample	*Thickness* (μm)	*Density* ($g\,cm^{-1}$)	*M. Pt.* (°C)	*Heat of fusion* ($J\,g^{-1}$)	$-CH_3/100C$ *From nmr*	$-CH_3/100C$ *From ir*[a]	$[-\overset{\wr}{\underset{\wr}{C}}-H]$ ($mole\,kg^{-1}$)[a]	$[-\overset{\wr}{\underset{\wr}{C}}CH_2CH_3]$[b] ($mole\,kg^{-1}$)	$[>C{=}CH_2]$ ($mole\,kg^{-1}$)
HDPE	28	0·958	129	173	—	0·1	0·08	≤0·1	0·10
LLDPE	105	0·925	109 (129)	93 (3)	—	1·7	1·2	0·53	0·019
LDPE	33	0·925	109	121	—	2·4	1·7	0·43	0·026
C_2H_4/6·2 mole % butene-1[c]	120	0·913	91	94	2·9	2·8	2·0	2·0	≤0·002
C_2H_4/6·0 mole % octene-1[c]	210	0·910	93	65	2·5	2·2	1·6	0	0·006
C_2H_4/7·1 mole % octadecene-1[c]	200	0·911	65	66	2·3	2·4	1·7	0	0·003
Polypropylene	25	0·889	160·5	89	33	33	24	0	—

[a] From the 1379 cm^{-1} FTIR absorption, assuming all CH_3 groups are in branches, ignoring the small contribution from CH_3 groups at backbone ends.
[b] From the 780 cm^{-1} FTIR absorption.
[c] Comonomer content from solution nmr.[10]

TABLE 2
γ-Initiated Oxidation of Branched Polyethylenes

Polyolefin	*Thickness* (μm)	[*Peroxyl*][a] (*mole kg*$^{-1}$) × 10^3	*Oxidation product*[b] (*mole kg*$^{-1}$)							
			Total [—*OOH*][c]	*Total* [—*OH*][d]	$>C{=}O^e$	$-C(=O^e)OH$	—*OOH*[f]		—*OH*[f]	
							sec.	*tert.*	*sec.*	*tert.*
HDPE	28	1·5	0·040	0·066	0·074	0·029	0·038	0	0·014	0
LLDPE	33	1·8	0·043	0·069	0·070	0·024	0·038	0	0·015	0·002
LDPE	105	1·8	0·043	0·074	0·078	0·029	0·040	0	0·014	0
C_2H_4/6·2 mole % butene-1	120	2·1	0·043	0·070	0·071	0·028	0·038	0·003	0·009	0·002
C_2H_4/6·0 mole % octene-1	210	2·1	0·039	0·068	0·051	0·036	0·029	0·003	0·010	0
C_2H_4/7·1 mole % octadecene-1	130	2·0	0·044	0·070	0·079	0·028	0·041	0·005	0·014	0·003
Polypropylene	25	2·5	0·41	0·39	0·242	0·033	0·070	0·31	0·005	0·018

[a] After 0·5 Mrad irradiation in air either at 77 K then held at −78°C or irradiated at −78°C.
[b] After 20 Mrad irradiation in air at ~40°C.
[c] From iodometry.
[d] From FTIR at 3400 cm^{-1}.
[e] From FTIR after SF_4 treatment.
[f] From FTIR after NO treatment.

radicals. The latter are indefinitely stable (at least for many days) at $-78°C$. These yields of peroxyl radicals are listed in Table 2. The yields are very close to those calculated from literature G-values, which predict $1{\cdot}7$–$2{\cdot}1 \times 10^{-3}$ mole kg^{-1} for 0·5 Mrad dose.[4,22]

The close similarity in the radical yields for all six PE films implies that they will also produce similar radical yields when γ-irradiated in air at ambient temperature. [Peroxyl radicals can be observed in polyolefins immediately after γ-irradiation at room temperature, but cannot be quantified because of their rapid decay.] The reproducible, higher peroxyl yield from PP implies more bond scission in highly branched molecules, as has been previously reported.[23]

Oxidation products may be directly observed by FTIR analysis of polyolefin films. However, several types of —OH species (alcohols and hydroperoxides) give broad, overlapped absorptions at $\sim 3400\,cm^{-1}$ and the absorptions of many carbonyl species merge together at 1780–$1700\,cm^{-1}$.[24] The use of NO and SF_4 gas treatments allows the more precise FTIR identification and quantification of alcohols and hydroperoxides (as nitrites and nitrates, respectively, after NO reaction), carboxylic acids (after SF_4 treatment to produce acid fluorides) and ketones (after removal of the overlapping acid absorptions and hydrogen bonding effects with —OH groups by SF_4 reactions).[12,13] The NO reaction products are particularly informative because of their intense absorptions (up to 4–7 times stronger than those of the original —OH species) and because primary, secondary and tertiary products have differing ir absorptions.[12]

Concentrations of oxidation products after γ-irradiation were observed both directly, and after reaction with NO and SF_4 for a wide range of γ-ray doses. For all of the polyolefins studied, product yields increased linearly with dose. This is shown for HDPE and LLDPE in Fig. 1. The absence of an induction period and the linearity indicate the complete absence of stabilization effects and of direct radiation attack on the oxidation products. For ease of comparison, product yields for all of the polyolefins studied after a 20 Mrad exposure are collected in Table 2. The —OOH yields from iodometry may also include some of the more reactive dialkyl peroxides and also peracids or peresters. Total —OH was obtained from the broad $3400\,cm^{-1}$ absorption. Only chain-end carboxylic acid groups (acid fluorides absorbing at $1848\,cm^{-1}$) were detected in the polyethylenes.[13] From PP, both chain-end and pendant ($1841\,cm^{-1}$) absorptions were found, but with the latter dominating.

From the study of a series of films differing in thickness, film thickness effects only became apparent at $\geq 250\,\mu m$ for a dose rate of 1 Mrad h^{-1}. For these thicker films, the oxidation rate was significantly slower than for thinner samples, presumably because of oxygen diffusion limitations.

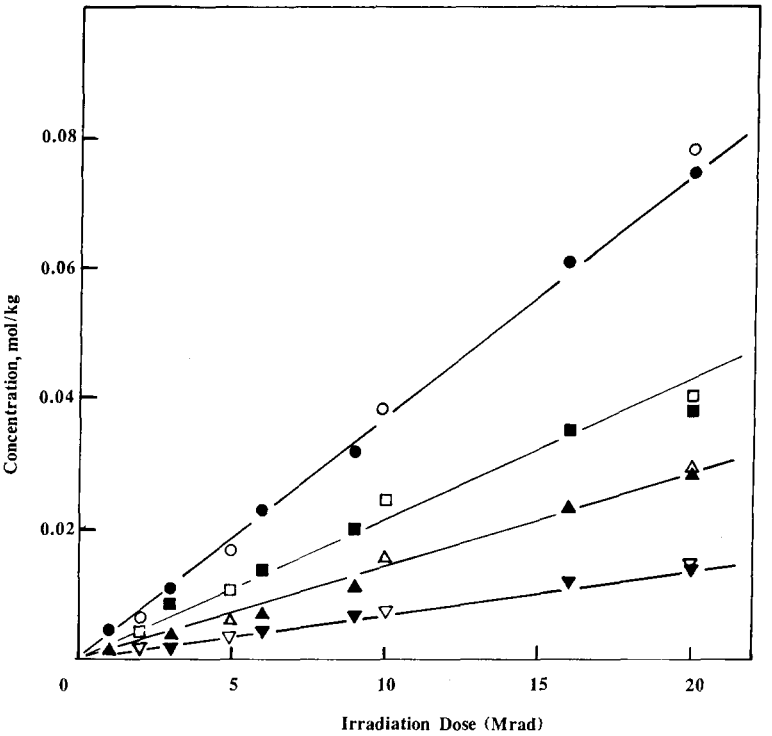


Fig. 1. Oxidation products from the γ-initiated oxidation of PE films. Closed symbols HDPE; open symbols LLDPE: ●, ○ Ketone (1718 cm^{-1}); ▲, △ Carboxylic acid (from 1846 cm^{-1} after SF_4 exposure); ■, □ Secondary hydroperoxide (as nitrate, after NO exposure); ▼, ▽ Secondary alcohol (as nitrite, after NO exposure).

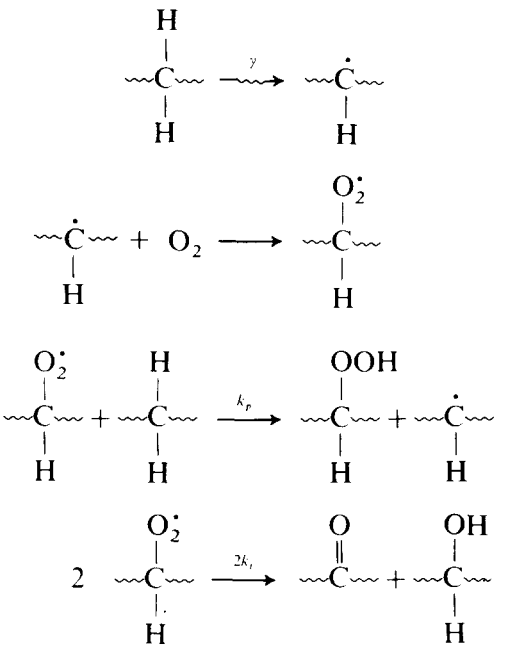
DISCUSSION

From a comparison of the concentrations of the respective oxidation products, very little systematic difference was found between the oxidative behaviour of any of the commercial polyethylenes or of the copolymers provided that they were stabilizer free. Thus, the overall rates of oxidation and individual rates of product formation appear to be quite insensitive to the frequency or length of side chain branching up to ~ 3 tert. C—H sites/100 carbons or of the vinyl unsaturation levels. Only for PP where every second carbon along the backbone carries a tert. C—H is there a dramatic difference in oxidation rate and product distribution.

The γ-initiated oxidation of PP gives a product mix which is quite consistent with that expected from the oxidation of model tert.-alkane liquids.[24] Predominantly tert. C—H attack occurs, although a detectable level of attack on sec. —C—H sites is also found (Table 2). Peroxyl radical

selectivity for the abstraction of tert. —C—H versus sec. —CH is ~7·4:1 at room temperature for model alkanes.[25] The detection of some pendant carboxylic acid groups is consistent with a little attack also on primary —C—H groups.

The oxidation of even the simplest PE (HDPE) is extremely difficult to rationalize in terms of the conventionally accepted reaction scheme (reactions 1–4).[24] The most important discrepancy is the significant yield of carboxylic acid groups. Occasional reference to acid group formation in oxidizing PE samples has been made, but their origin and implications have not been identified.[25,26] These groups *must* come from chain scission; ketonic species in PE are not backbone scission products (*cf.* reaction (4)). In fact, even the oxidation of sec. —CH sites in model hydrocarbons only follows the simple oxidative kinetic scheme in the earliest stages ($\leq$0·5% conversion).[27]



The virtual absence of an effect of tert. —CH sites on the oxidation of polyethylenes when the rate of initiation is constant should not really come as a surprise. At the highest level of tert. C—H sites (~3/100 carbons) in our commercial and laboratory samples, the relative rates for peroxyl attack on a secondary C—H site as compared to a tert. C—H site are ~10:1 [k_p(sec C—H)/k_p(tert. C—H) = 1/7·4 at room temperature].[25] By use of high resolution nmr, Cheng *et al.* have found some attack at tert.-sites in LDPE samples, but only after very high levels of oxidation (~2 mole kg^{-1} total

oxidation).[28] The small yields of tert.-products detected for several copolymers (Table 2) are consistent with a 10:1 ratio of sec. C—H attack to tert. C—H attack.

Some other literature data on polyolefin oxidation also point to the absence of an effect of low levels of branching. Shilov and Denisov have reported identical thermal oxidation rates at ~116°C for a series of C_2H_4/C_3H_6 copolymers when initiated by a high concentration of added peroxide.[6] Quite recently, two Japanese groups have presented some data on the γ-oxidation of a range of polyethylenes and again shown little effect of branching.[7,8] Unfortunately, little information was given on the type of branching present or on the precise nature of the oxidation products.

The high crystallinity in the HDPE film as compared to the other PE samples (indicated by both density and heat of fusion) might be expected to lead to a lower rate of oxidation if it is assumed that oxidation only proceeds in the amorphous phase. However, the esr data indicates that virtually all of the radicals generated from the γ-irradiation of all of the PE samples convert to peroxyl radicals and that their concentration is the same for all samples. This implies either that all macro alkyl radicals are in O_2-accessible regions (e.g. because the 'crystals' contain sufficient defects to be O_2-permeable) or that these sites migrate quickly (even at −78°C) into the amorphous region.

As mentioned in the Introduction, photo- and thermally initiated oxidations may be very different for linear and branched PE samples. In fact, xenon arc irradiation led to a rate of oxidation as measured by ketonic product accumulation which was 3–4 times faster for our LLDPE than for HDPE. This difference must reflect differences in photo-initiating impurity levels.

EFFECT OF A PHENOLIC ANTIOXIDANT

One of the C_2H_4/butene-1 samples was pressed into film and then γ-irradiated without prior extraction to remove the storage stabilizer [AOX: octadecyl β-(2,6-di-t-butylphenol)propionate, concentration 0·014 mole kg^{-1}]. Prior to irradiation, the ester absorption of AOX in the film was clearly visible at 1742 cm^{-1} together with its absorptions at 1237 and 1160 cm^{-1} and the phenol absorption at 3652 cm^{-1}. The ester absorption was reduced to ~50% by 20 Mrad exposure, implying some radiation-induced cleavage of the ester bridge. The phenolic —OH absorption, the 1237 and the 1160 cm^{-1} absorptions were destroyed completely after only 5 Mrad, and an interesting new series of ir absorptions detected at the same time. These included the growth and then loss of 1650 and 1670 cm^{-1}

absorptions. These absorptions are entirely consistent with those reported by Kovarova-Lerchova and Pospisil and attributed to the intermediacy of a 4-alkylperoxycyclohexa-2,5-dienone.[29] This unstable product results from the scavenging of two peroxyl radicals by AOX.

Polyethylene samples containing phenolic antioxidants showed a distinct induction period in product formation. Only extracted samples were linear in product formation with increasing dose, as shown in Fig. 1.

CONCLUSIONS

The intrinsic rate of oxidation of polyethylene and the composition of its oxidation products are virtually independent of the presence of backbone branching, whether short or medium length, at levels found in commercial materials. Polyethylene oxidation cannot, however, be explained in terms of a simple free-radical chain reaction. In particular, the presence of carboxylic acid end groups formed by oxidative chain scission must be further explored.

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