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Dicarboxylic Acids and Ketoacids Formed in Degradable Polyethylenes by Zip Depolymerization through a Cyclic Transition State

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ABSTRACT: The intermediate and final degradation products formed in six different low-density polyethylene (LDPE) films modified with either starch and/or pro-oxidants or photosensitizers (Scott−Gilead formulation [SG]) were investigated. We propose that dicarboxylic acids and ketoacids, formed in the materials to varying degrees, are due to both secondary oxidation products and a zip depolymerization mechanism by backbiting through a cyclic transition state. Hydrocarbons, ketones, carboxylic acids and dicarboxylic acids are formed during early stages of photo-oxidation, and the ketones disappeared while several ketoacids appeared and the relative amount of dicarboxylic acids increased in the most severely degraded materials. During prolonged photo-oxidation, additional oxidation of ketones and monocarboxylic acids to dicarboxylic acids explains the high amount of dicarboxylic acids. In the thermo-oxidized samples the amount of ketones and monocarboxylic acids remained high even in the most degraded samples. Mono- and dicarboxylic acids were formed in several micrograms per 100 mg of polymer, while the ketones and ketoacids were formed in fewer micrograms per 100 mg of polymer. LDPE modified with the iron dimethyldithiocarbamate (SG1) was the most susceptible material to photo-oxidation, while LDPE containing starch and pro-oxidants (LDPE-MB) was the most susceptible material to thermo-oxidation. Degraded LDPE-MB demonstrated less formation of degradation products; *e.g.*, only in UV-initiated samples thermally degraded at 80 °C for 5 weeks could degradation products be detected. Larger amounts of ketones and ketoacids were formed in the SG materials than in the starch-filled materials.

1. Introduction

The environmental degradation of polyethylene (PE) is a complex process, where several degradation mechanisms interact while working toward the total destruction of the material. After the molecular weight of PE has been reduced by photo degradation and/or thermal degradation, low molecular weight polymers are formed and then biodegraded. Studies show that microorganisms are able to assimilate the oxidation products formed during thermo- and photo-oxidation of polyethylene.[1,2]

There are several ways to enhance the environmental degradation of polyethylene. Increased photodegradability is obtained by copolymerization of carbonyl groups directly into the backbone (ethylene/carbon monoxide) or in the side chains (vinyl ketone copolymers) of the polyethylene. Another way to increase the photodegradability is to add photosensitizing additives, like organosoluble metal ions or sulfur-complexed metal ions (Scott−Gilead formulation). A wide range of embrittlement times is achieved by using different protective and sensitizing additives.[3−5] Thermal degradation and/or photodegradation is enhanced if prooxidants containing transition-metal ions are used alone or together with starch (Griffin process). Some transition-metal compounds, *e.g.*, iron and manganese, have a powerful catalytic effect on radical formation from hydroperoxides leading to rapid molecular weight reduction by breakdown of the intermediate alkoxyl radicals. In earlier studies we have followed the spectroscopic and mechanical changes in low-density polyethylene (LDPE) modified by Griffin[6,7] and Scott−Gilead formulations.[8] We have also identified thermal degradation products formed in LDPE modified by pro-oxidants and/or starch.[9−11]

The objective of the present paper is to compare degradation products formed during photo-oxidation and low-temperature thermo-oxidation in different degradable polyethylenes containing oxidizable and/or biodegradable additives. The degradation product patterns in the materials allow a mechanism to be proposed for the formation of ketoacids and dicarboxylic acids. Polyethylenes modified according to the Griffin process (pro-oxidants and starch) and the Scott−Gilead formulation (photosensitizing additives) are analyzed. In addition, the degradation rate and molecular weight changes are compared and correlated with the identified degradation products.

2. Experimental Section

2.1. Materials. The starch-filled materials were made by a conventional blown film process of a LDPE grade of MFI 2 acquired from ATO (France). The 30 μm thick films were modified with 20% masterbatch (LDPE-MB) or with 7.7% corn starch (LDPE-starch) to promote the degradation. The masterbatch consists mostly of corn starch (7.7%), styrene−butadiene copolymer (SBS), manganese stearate, and linear low-density polyethylene (LLDPE). Three polyethylenes made by the Scott−Gilead process containing photosensitizing additives were also studied. The additives were (1) iron dimethyldithiocarbamate (SG1), (2) iron dimethyldithiocarbamate and 0.8% carbon black (SG2), and (3) iron dimethyldithiocarbamate and nickel dibutyldithiocarbamate (SG3). The film thicknesses were 27.5, 26, and 21 μm, respectively. The photosensitized materials were a gift from the late professor D. Gilead. In addition, a 30 μm thick polyethylene film (LDPE) without additives was analyzed.

2.2. The Degradation Procedure. Different polyethylene films were photo-oxidized in an Atlas UVCON weatherometer equipped with UV lamps (FS-40 fluorescent sunlamp)

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giving radiation with wavelengths between 280 and 359 nm. During the irradiation the temperature increased to a mean value of about 50 °C. Samples were irradiated for different amounts of time up to 300 h. The same materials were also subjected to thermal aging at 80 °C in sealed vials to collect the low molecular weight degradation products formed during the thermo-oxidation. One series of samples was thermally aged for 5 weeks at 80 °C, while in another series the induction period was surpassed by 100 h of UV radiation before the thermal treatment.

2.3. The Extraction Procedure. The products were extracted from the films with 1 mL of diethyl ether. After 1 h the diethyl ether was separated from the remaining polymer films and evaporated to dryness. The products were then dissolved in 50 μL of hexane. The hexane fraction was removed, and the hexane-insoluble products were dissolved in 50 μL of 0.1% HCl in methanol. The 0.1% HCl in methanol fraction was warmed for 15 min at 60 °C to methylate ketoacids and dicarboxylic acids.

2.4. Gas Chromatography−Mass Spectrometry (GC−MS). The samples were analyzed with a Varian gas chromatograph coupled to a Finnigan SSQ7000 mass spectrometer. The column used was a DB-WAX capillary column from J&W (30 m × 0.32 mm i.d.). The column temperature was held for 1 min at 60 °C, raised to 240 °C at 10 °C/min, and then held for 8 min at 240 °C. Helium was used as a carrier gas. The samples were introduced in the splitless injection mode at 225 °C.

2.5. High-Temperature Size-Exclusion Chromatography (HT-SEC). A Waters 150C high-temperature SEC equipped with two PL gel, 10 μm mixed-B columns from Polymer Laboratories and an RI detector was used to measure the molecular weights and distributions. The mobile phase was 1,2,4-trichlorobenzene (TCB) at 135 °C, and the flow rate was 1 mL/min. The calibration was performed according to polystyrene standards.

2.6. Fourier Transform Infrared Spectroscopy (FTIR). FTIR analysis was performed on a Perkin-Elmer 1760 infrared Fourier transform spectrometer with a 4× beam condenser. To use the attenuated total reflection technique (ATR), the instrument was equipped with a micro ATR holder and a KRS-5 prism with an incident angle of 45°. On the IR spectra special interest was focused on the carbonyl region. Carbonyl absorbance at 1718 cm^{-1} relative to the CH_2 scissoring peak at 1463 cm^{-1} was measured.

3. Results and Discussion

Depending on the application, degradable materials with different degradation times and mechanisms are required. The choice of additives renders the same polymer to be sensitive toward different environmental factors (*e.g.*, hyrolysis, oxidation, biodegradation) and to have different degradation times. LDPE-starch and LDPE-MB are designed to be used as compostable packaging materials. SG1 is a fast-degrading system for packaging, whereas SG2 and SG3 are intended for agricultural films and fibers. SG3 is a “time-controlled” system which has an induction time before photo-oxidation.

3.1. Analysis of the Degradation Products. The low molecular weight degradation products remaining in the polyethylene films after different photo- and thermo-oxidation times were extracted and analyzed by GC−MS. Figures 1 and 2 show the GC−MS chromatograms of the low molecular weight products extracted from the SG1 films. Mono- and dicarboxylic acids, hydrocarbons, ketones, and ketoacids were identified in all materials, but in varying numbers and amounts. Dicarboxylic acids were the main products in the most severely photo-oxidized samples. Mono- and dicarboxylic acids were the main products after thermo-oxidation, but also the amount of ketones and ketoacids was higher compared to the amount formed by photo-oxidation.

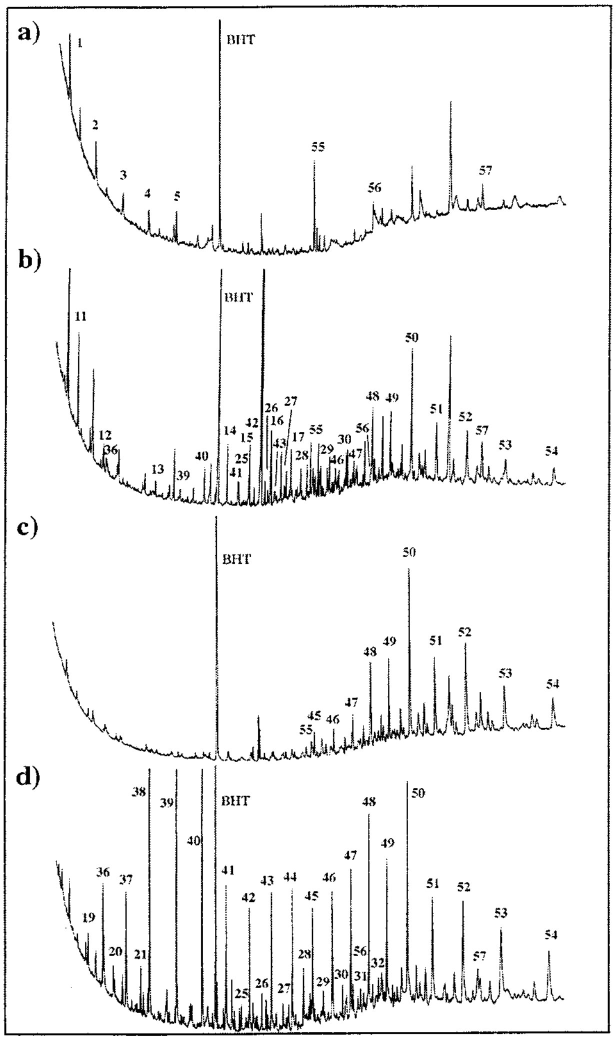


Figure 1. Degradation products formed in the SG1 films after different aging times. GC−MS chromatograms of the hexane fraction after (a) 0, (b) 100, and (c) 300 h of UV irradiation and (d) after 100 h of UV irradiation followed by 5 weeks at 80 °C.

Ketones were identified in SG1 and SG2 films only after 100 h of UV radiation. After 300 h several ketones were formed also in SG2, SG3, and pure LDPE, but no ketones were found in SG1, LDPE-starch, and LDPE-MB films. The absence of ketones in the most degraded SG1 films indicates further oxidation of the ketones identified after 100 h to other products such as ketoacids or dicarboxylic acids. A homologous series of ketoacids was formed in the SG1 and SG2 films after 300 h of photo-oxidation, while in most of the other materials only 4-oxopentanoic acid was formed after the same treatment.

After thermo-oxidation a homologous series of 2-ketones was identified in all the materials and a homologous series of ketoacids was identified in LDPE-starch, SG1, SG2, and SG3. Larger amounts of ketones and ketoacids were formed in the SG materials than in the LDPE and starch-modified materials.

The number and amount of degradation products formed in LDPE-MB were generally lower compared to the other materials. If the thermal degradation was not initiated by UV radiation, then degradation products were only formed in LDPE-MB during 5 weeks at 80 °C. These products were similar to those identified after

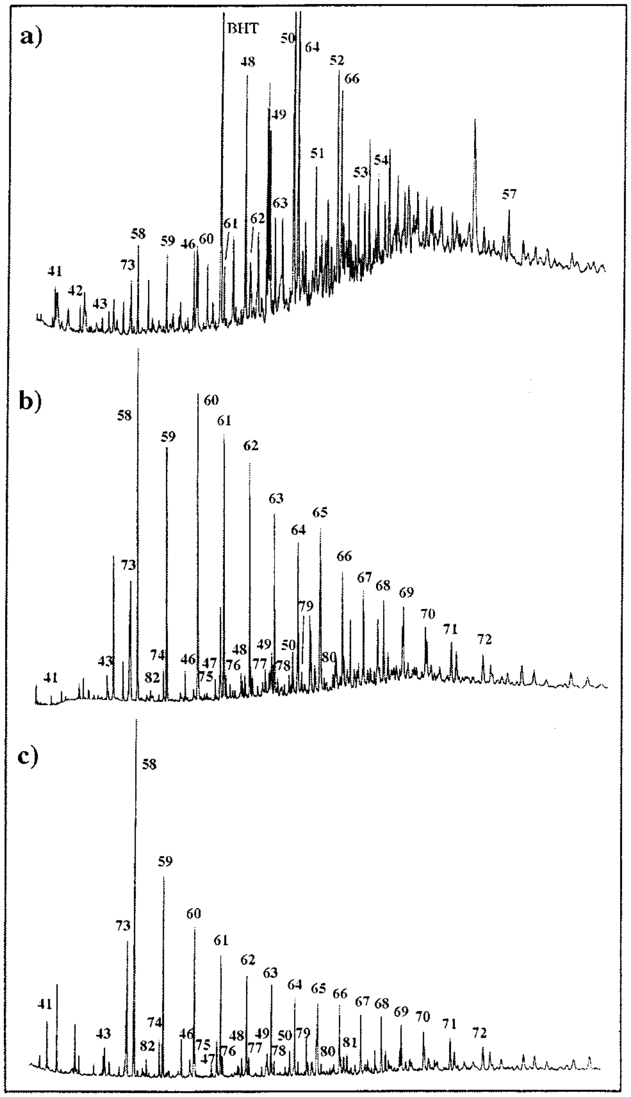


Figure 2. Degradation products formed in the SG1 films after different aging times. GC–MS chromatograms of the methanol fraction after (a) 100 and (b) 300 h of UV irradiation and (c) after 100 h of UV irradiation and 5 weeks at 80 °C.

UV-initiated thermo-oxidation and included homologous series of mono- and dicarboxylic acids, ketoacids, ketones, and alkanes.[9] Table 1 gives the products identified after photodegradation and UV-initiated thermal degradation. Exact quantification of each product was not done, but in general most of the ketones and ketoacids were formed in less than micrograms levels per 100 mg of polymer, while several micrograms of the most abundant mono- and dicarboxylic acids were formed. The phthalates are most likely external impurities from the extraction step.

3.2. Molecular Weight Changes. Figure 3 shows molecular weights and molecular weight distributions after different photo-oxidation times. Although the pro-oxidant formulation containing manganese-stearate was earlier found to be an effective promoter of thermal degradation at low temperatures,[11,12] it did not substantially accelerate the photodegradation rate of LDPE-MB in comparison to pure LDPE and LDPE modified with starch. The number-average molecular weight (M_n) of LDPE, LDPE-starch, and LDPE-MB decreased at almost equal rates during the UV radiation. A somewhat larger difference was seen in the weight-average molecular weights (M_w). LDPE-MB degraded slightly faster than LDPE-starch, which in turn degraded somewhat faster than pure LDPE.

The materials containing photosensitizers demonstrated larger differences in the degradation behavior. The M_n and M_w of SG1 containing iron dimethyldithiocarbamate started decreasing almost immediately when subjected to UV radiation, while SG2 had a longer induction period and showed only a moderate molecular weight decrease during the first 50 h (Figure 3). The M_n of SG2 demonstrated the fastest decrease between 50 and 100 h, after which the degradation rate again slowed down. SG3 had the longest induction period, and it was the only material that showed M_n increase during the first 100 h. SG1 degraded initially faster than the other materials, but after 300 h all the materials, except SG3, had come down to almost the same molecular weight. SG3 films that contained both iron dimethyldithiocarbamate and nickel dibutyldithiocarbamate degraded considerably slower than the other materials during the whole experiment.

M_z and MWD of LDPE-MB, LDPE-starch, and LDPE increased during the first 50 h, after which M_z started decreasing and MWD narrowed as seen in parts c and d of Figure 3. This indicates that cross-linking takes places during the initial stages of degradation. While the maximum of the molecular weight distributions shifted to lower molecular weights, the cross-linking was seen as a formation of a shoulder on the high molecular weight side of the SEC chromatograms. This small shoulder had disappeared after 300 h of UV radiation. The MWD of SG1 broadened during the first 100 h and narrowed then on prolonged radiation. The M_z of SG1 and SG2 decreased steadily during the whole experiment. No shoulder was seen in the SEC chromatograms of the SG2 material, nor did the MWD broaden notably. The M_z of SG3 decreased originally but started increasing between 50 and 100 h. These results indicate that less cross-linking takes place in the Scott–Gilead materials, especially in SG2, than in the starch-filled materials. All the materials, however, remained totally soluble, as is generally the case when main-chain scission dominates over the molecular enlargement reactions.

Table 2 gives the molecular weights and molecular weight distributions after thermal and UV-initiated thermal aging at 80 °C. The molecular weight of LDPE-MB decreased rapidly during 5 weeks at 80 °C, while the molecular weight of the other materials remained almost constant (LDPE, LDPE-starch, and SG2) or increased slightly (SG1 and SG3). If the induction period was surpassed by subjecting the materials to 100 h of UV radiation, the molecular weight of all the materials continued decreasing during the following thermal aging at 80 °C. The molecular weight of LDPE, LDPE-starch, LDPE-MB, SG1, and SG2 decreased rapidly during 100 h of irradiation. When 100 h of photo-oxidation was followed by 5 weeks at 80 °C, the further degradation was moderate in the case of LDPE, LDPE-starch, LDPE-MB, and SG1, while a significant reduction in molecular weight was seen in SG2 and SG3. Even though the molecular weight of SG3 increased during the UV treatment, the induction period was surpassed and the molecular weight decreased rapidly during the following thermal treatment.

LDPE-MB that was originally very sensitive to thermal aging decreased less in molecular weight than LDPE and LDPE-starch during the UV-initiated thermal aging. The manganese stearate in the pro-oxidant

Table 1. Low Molecular Weight Degradation Products Identified in the Different Materials after Photo-oxidation and UV-Initiated Thermal Degradation at 80 °C[a]

		LDPE				LDPE-starch				LDPE-MB				SG1				SG2				SG3			
		0h	100h	300h	*	0h	100h	300h	*	0h	100h	300h	*	0h	100h	300h	*	0h	100h	300h	*	0h	100h	300h	*
HYDROCARBONS																									
1	tridecane	s	s	s		s	s			s				s				s	m	s	s	s	s		
2	tetradecane	s	s	s		s	s		s	s	s			s				m	s	s		s		s	
3	pentadecane	s	s	s		s	s		s	s	s		s	s				s	s	s		s	s	s	
4	hexadecane	s	s	s		s	s			s	s		s	s				s	s	s		s	s	s	
5	heptadecane	s	s	s		s	s			s	s		s	s				s	s	s		s	s	s	
6	octadecane	s	s	s		s	s		s	s	s		s	s				s	s	s		s	s	s	
7	nonadecane									s												s			
8	eicosane	s	s			s	s		s	s	s		s	s			s		s			s	s	s	
9	heneicosane								s	s			s				s								
10	docosane	s	s			s	s		s	s	s		s				s			s					
11	1-tridecene		s	s											s			s	s	s		s	s		
12	1-tetradecene		s	s						s					s			s	s	s		s	s		
13	1-hexadecene														s			s	s			s			
14	1-nonadecene		s	s	s		s				s				s					s				s	
15	1-eicosene		s	s	s		s			s	s				s					s				s	
16	1-heneicosene		s	s	s		s				s				s					s				s	
17	1-docosene		s	s	s		s			s	s				s					s				s	
KETONES																									
18	2-octanone				s																s				s
19	2-nonanone				s				s								s				s				s
20	2-decanone				s				s								s				s				s
21	2-undecanone				s				s								s				s				s
22	2-dodecanone				s				s								s				s				s
23	2-tridecanone				s				s								s				s				s
24	2-tetradecanone				s				s				s				s				s				s
25	2-pentadecanone				s				s								s			s	s			s	s
26	2-hexadecanone			s	s				s				s		s		s		s	s	s			s	s
27	2-heptadecanone			s	s				s				s		s		s		s	s	s			s	s
28	2-octadecanone			s	s				s				s		s		s		s	s	s		s	s	s
29	2-nonadecanone			s	s				s				s		s		s		s	s	s			s	s
30	2-eicosanone			s	s				s				s		s		s		s	s	s			s	s
31	2-heneicosanone				s				s						s		s			s	s			s	s
32	2-docosanone				s				s						s		s			s	s				
33	2-tricosanone				s				s																
34	2-tetracosanone				s				s																
35	2-pentacosanone				s				s																
CARBOXYLIC ACIDS																									
36	acetic acid				m				s								s				s				m
37	propanoic acid				s				s								s				m				m
38	butanoic acid				l				m								l			s	l			s	l
39	pentanoic acid		s		l				m				s		s		l		s	s	xl				l
40	hexanoic acid		s	s	m				m				s		s		m		s	s	l		s	s	l
41	heptanoic acid				m				s				s				m			s	m			s	l
42	octanoic acid		s		m				s				s				m		s	s	m				m
43	nonanoic acid		s		m				s				s		s		m		s		m				m
44	decanoic acid		s		m				s				s		s		m			s	m				l
45	undecanoic acid		s		m				s				s			s	m				m				l
46	dodecanoic acid		s		m			s	s			s	s		s	s	m		s	s	m			s	m
47	tridecanoic acid		s	s	m				s				s		s	s	m			s	m			s	m
48	tetradecanoic acid		s	s	m		s	s	s		s	s	s		s	s	m		s	s	m		s	s	m
49	pentadecanoic acid		s	m	m			m	s		s	s	s		s	s	m		s	s	m		s	s	m
50	hexadecanoic acid		m	m	l		s	l	s		s	m	s		m	m	m		s	m	m		s	s	l
51	heptadecanoic acid		s	m	m		s	l	s		s	s	s		m	m	m		s	m	m		s	s	l
52	octadecanoic acid		s	m	m		s	l	s		s	m	s		m	m	m		s	m	m		s	s	l
53	nonadecanoic acid		s	m	m			m	s			s	s		s	s	m			s	m			s	m
54	eicosanoic acid		s	s	m			m	s				s		s	s	s			s	s			s	m
PHTHALATES																									
55	diethyl phthalate	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
56	dibutyl phthalate	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
57	di(2-ethylhexyl)phth.	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
DICARBOXYLIC ACIDS																									
58	butanedioic acid		s	l	s		s	m	m		m	l	s		s	xl	l		s	m	l		s	s	l
59	pentanedioic acid		s	l	s		s	m	s		s	m	s		s	xl	l		s	m	l		s	s	m
60	hexanedioic acid		s	l	s		s	m	s		s	m	s		s	xl	l		s	m	l		s	s	m
61	heptanedioic acid		s	l	s		s	l	s		s	m	s		s	xl	m			m	m			s	m
62	octanedioc acid		s	l	s		s	l	s		s	m			s	xl	m			l	m		s	s	s
63	nonanedioic acid		s	l	s		s	l	s		s	m	s		s	xl	m		s	l	m		s	s	s

Table 1 (Continued)

	LDPE				LDPE-starch				LDPE-MB				SG1				SG2				SG3			
	0h	100h	300h	*	0h	100h	300h	*	0h	100h	300h	*	0h	100h	300h	*	0h	100h	300h	*	0h	100h	300h	*
64 decanedioic acid		m	l	s		s	l	s		s	l	s		l	xl	m		s	l	m		s	s	s
65 undecanedioic acid		s	l	s		s	l	s		s	m	s		s	xl	m			l	m		s	s	m
66 dodecanedioic acid		m	l	s		s	l	s		s	m	s		m	l	m		s	l	m		s	s	s
67 tridecanedioic acid			l	s			l	s		s	m				l	m			l	m			s	s
68 tetradecanedioic acid			l	s			l	s			m				l	m			l	m			s	s
69 pentadecanedioic acid			l				m	s			m				l	s			l	m			s	s
70 hexadecanedioic acid			l				l	s			s				l	s			l	m			s	s
71 heptadecanedioic acid			l				l	s			m				l	s			m	m			s	s
72 octadecanedioic acid			l				m	s			s				l	s			m	s			s	s
KETOACIDS																								
73 4-oxopentanoic acid		s	s	s			s	s		s	s	s		s	l	s		s	s	m			s	s
74 5-oxohexanoic acid			s	s				s				s			m	s			s	s				s
75 6-oxoheptanoic acid								s							s	s			s	s				s
76 7-oxooctanoic acid			s					s							m	s			s	s				s
77 8-oxononanoic acid								s							m	s			s	s				s
78 9-oxodecanoic acid								s							s	s			s	s				s
79 10-oxoundecanoic acid								s							m	s			s	s				s
80 11-oxododecanoic acid								s							s	s			s	s				s
81 12-oxotridecanoic acid								s							s	s				s				s
82 2-oxopentanedioic acid			s					s							s	s			s	s				s

[a] * = 100 h of UV radiation followed by thermal aging for 5 weeks at 80 °C. Relative area of the peak. s = 1−20, m = 21−50, l = 51−150, x1 = 151−∞. s = less than 1 μg/100 mg of polymer; m, l, and xl = over 1 μg/100 mg of polymer.

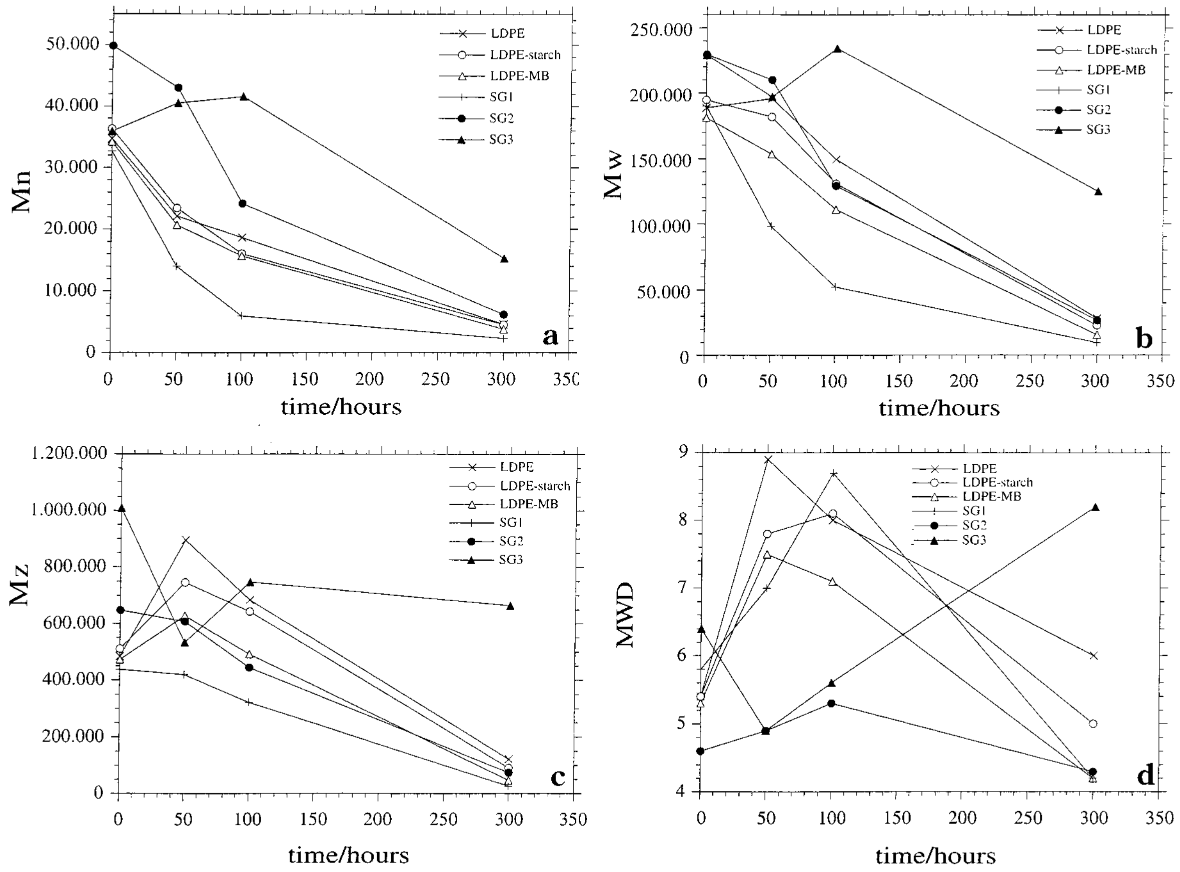


Figure 3. (a) Number-average molecular weights, (b) weight-average molecular weights, (c) M_z and (d) molecular weight distributions of different materials as a function of irradiation time.

formulation of LDPE-MB films that initially was a very effective accelerator of thermal degradation was either used up or deactivated in some other way during the UV radiation, and it could no longer promote the thermal degradation. This deactivation was so effective that the LDPE-MB films subjected to 100 h of irradiation before the thermo-oxidation for 5 weeks at 80 °C had higher molecular weight than the films that were only subjected to thermal aging for 5 weeks at 80 °C.[9] The M_z values of all the materials decreased and MWDs narrowed during the thermal aging.

3.3. Carbonyl Index. The different carbonyl groups formed during oxidation of the LDPE materials (*e.g.*, carboxylic acids, aldehydes, esters, ketones, and lactones) are more concentrated at the surface layers, because more oxygen is available near the surface. Reflection FTIR gives useful information about the surfaces of degraded polymers, providing results on in particular the initial product formation. Figure 4 shows the carbonyl absorbance measured at 1718 cm^{-1} as a function of irradiation time for the different materials. The concentration of carbonyl groups at the surface

Table 2. Molecular Weights and Molecular Weight Distributions at the Beginning, after 5 Weeks at 80 °C, after 100 h of UV, and after 100 h of UV Radiation followed by 5 weeks at 80 °C

material	degradation procedure	M_n	M_w	M_z	MWD
LDPE	unaged	34 700	189 000	485 000	5.4
	5 weeks at 80 °C	35 900	186 000	486 000	5.2
	100 h of UV	18 700	149 000	684 000	8.0
	100 h of UV + 5 weeks at 80 °C	12 700	62 400	223 800	4.9
LDPE-starch	unaged	36 300	195 000	511 000	5.4
	5 weeks at 80 °C	33 400	195 000	511 000	5.8
	100 h of UV	16 100	131 000	643 000	8.1
	100 h of UV + 5 weeks at 80 °C	11 000	49 100	181 000	4.5
LDPE-MB	unaged	34 200	181 200	473 000	5.3
	5 weeks at 80 °C	8 000	29 400	83 100	3.7
	100 h of UV	15 700	111 000	492 000	7.1
	100 h of UV + 5 weeks at 80 °C	14 800	50 300	131 000	3.4
SG1	unaged	32 700	190 000	438 000	5.9
	5 weeks at 80 °C	46 000	202 000	464 000	4.4
	100 h of UV	6 000	52 300	321 000	8.8
	100 h of UV + 5 weeks at 80 °C	4 800	23 100	110 000	4.8
SG2	unaged	49 800	230 000	648 000	4.6
	5 weeks at 80 °C	48 900	226 000	652 000	4.6
	100 h of UV	24 200	129 000	444 000	5.3
	100 h of UV + 5 weeks at 80 °C	7 500	24 800	66 300	3.3
SG3	unaged	35 900	229 000	1 010 000	6.9
	5 weeks at 80 °C	44 300	200 000	534 000	4.5
	100 h of UV	41 600	234 000	748 000	5.6
	100 h of UV + 5 weeks at 80 °C	10 300	36 500	114 300	3.5

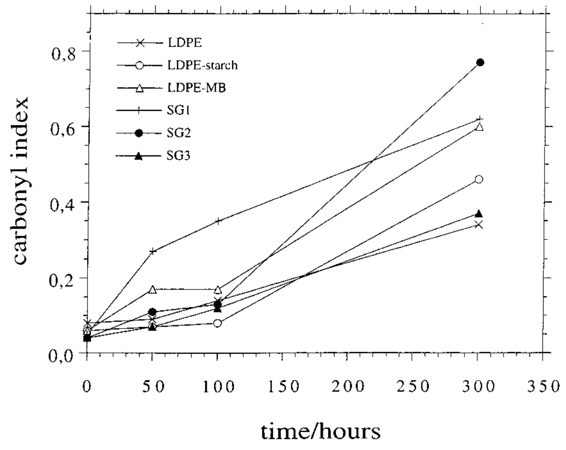


Figure 4. Carbonyl index after different photo-oxidation times.

increases at prolonged irradiation times. During the first 50 h the carbonyl index of SG1 increased faster than the carbonyl index of the other materials. LDPE-MB showed the second rapid increase, while the carbonyl index of the other materials remained almost constant during the first 100 h. After the initial slow increase during the first 100 h of irradiation, the carbonyl index of SG2 increased rapidly, and after 300 h, it had the highest carbonyl index followed by SG1 and LDPE-MB.

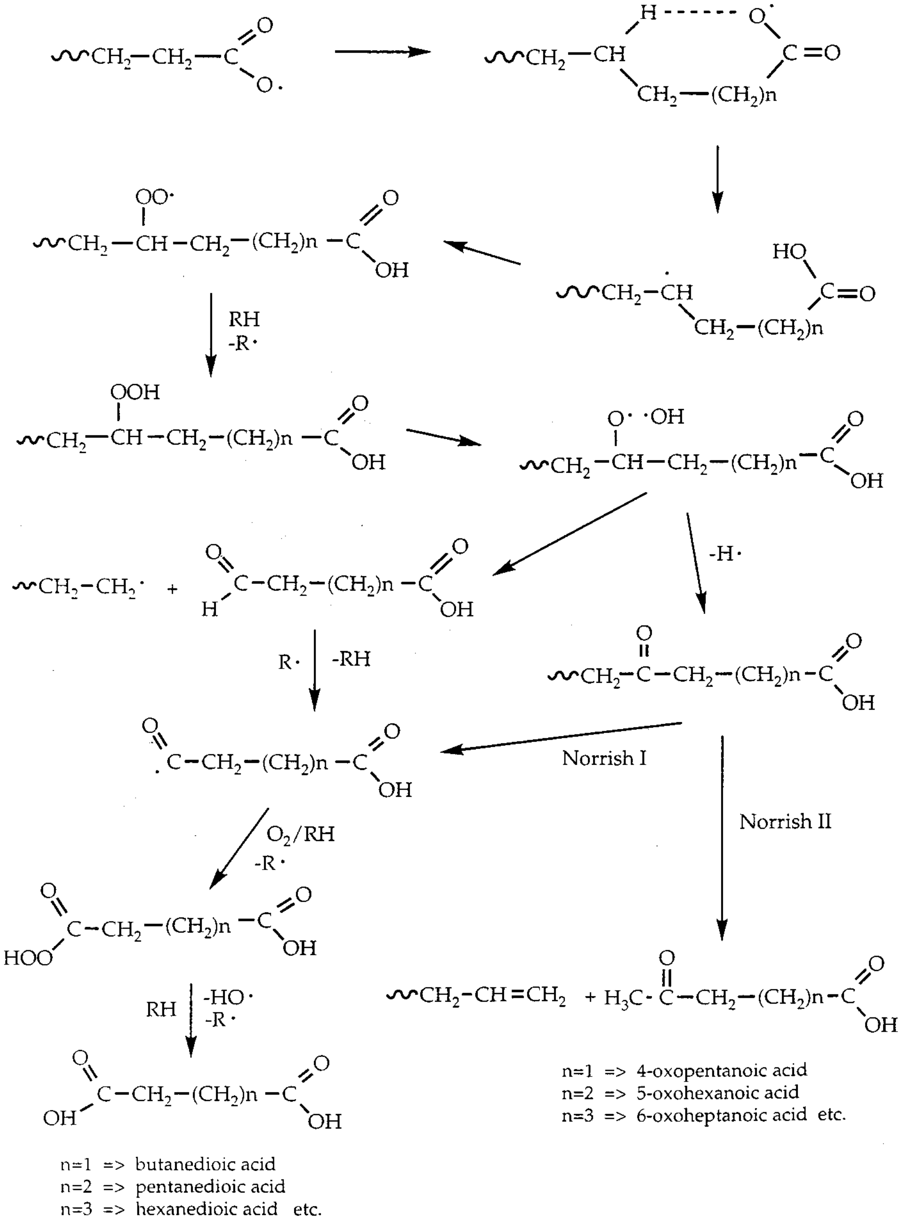
3.4. Correlation of the Degradation Products to the Molecular Weight and Carbonyl Index. There was a good correlation between the molecular weights and carbonyl index. The samples that showed the largest decrease in molecular weight had the highest carbonyl index. The amount of products formed agreed generally well with changes in the molecular weight and carbonyl index. Photo-oxidation of the Scott−Gilead materials gave, however, larger amounts of low molecular weight products than the amounts formed in LDPE, LDPE-starch, and LDPE-MB. This correlates with the higher cross-linking density seen in the starch-filled materials, which lowers the possible amount of low molecular weight products that may be formed. SG1 had lower molecular weight than the other materials after 100 and 300 h of UV radiation, and more degradation products were also formed in the SG1 films. The amount of dicarboxylic acids increased more than the amount of other products, especially in the severely photo-oxidized films. Largest amounts of dicarboxylic acids were formed in the material that had degraded to the lowest molecular weight, *i.e.*, SG1 after 300 h of UV radiation. In the Scott−Gilead materials larger amounts of ketones and ketoacids were formed during thermal aging for 5 weeks, compared to the starch-filled materials and LDPE when they had reached the same level of degradation.

Almost equal amounts of mono- and dicarboxylic acids were identified in the most degraded materials, SG1 and SG2, when the materials were subjected to thermo-oxidation at 80 °C after 100 h of UV radiation. The carboxylic acids were, after the same treatment, the main products in SG3, LDPE, LDPE-starch, and LDPE-MB. The amounts of ketones and ketoacids were larger than those after the photo-oxidation, and larger amounts of products were formed in the Scott−Gilead materials compared to the starch-filled materials and LDPE, which is in agreement with the larger molecular weight decrease of SG1, SG2, and SG3.

3.5. Mechanism for the Formation of Degradation Products. Girois *et al.* suggested recently that 2-methyl-4-oxopentanoic acid is formed during photo-oxidation of polypropylene by a backbiting process that propagates along the macromolecule chain.[13] In Scheme 1, we propose a similar zip depolymerization mechanism for the formation of both dicarboxylic acids and keto-acids from polyethylene by backbiting through a cyclic transition state. A carboxyl radical at the end of the polyethylene chain formed either by decomposition of a secondary hydroperoxide followed by β-scission or by reaction of a primary alkyl radical at the chain end with oxygen can abstract a hydrogen intramolecularly from the same chain to form a carboxyl group and a secondary macroradical. The secondary alkyl radical can further react with oxygen to form a secondary hydroperoxide.

As a result of the hydroperoxide decomposition, oxygen-containing groups are formed in the polyethylene

Scheme 1. Mechanism for the Formation of Dicarboxylic Acids and Ketoacids by Zip Depolymerization through a Cyclic Transition State



chain. The secondary alkoxyl radicals (RO•) formed by homolysis of the peroxide bonds can form polymeric ketones or undergo β-scission which will cause a backbone scission and generate a primary alkyl radical and an aldehydic chain end. The secondary alkoxy radical can also H-abstract to form a secondary alcohol. The polymeric ketone may undergo either Norrish I or Norrish II types of reaction to form either a dicarboxylic acid and a primary hydrocarbon radical or a ketoacid and an unsaturated chain end, respectively. Even though Norrish II type of reaction is generally several times more abundant than Norrish I type of reaction, more carboxylic acids than ketones were formed in our study. Ketones formed by Norrish II types of reaction absorb radiation above 300 nm and can be converted to carboxylic acids on prolonged irradiation. Also aldehydes and secondary alcohols can be further oxidized to carboxylic acids. Carboxylic acids are the most stable oxygen-containing products. They do not absorb radiation above 300 nm, and they accumulate when other oxygen-containing products are oxidized to carboxylic acids. Dicarboxylic acids and ketoacids can also be formed from short-chain carboxylic acid radicals through a similar cyclic transition state.

Both butanedioic acid and 4-oxopentanoic acid are formed by a six-membered transition state which is energetically more favorable than both smaller or larger cyclic transition states. Their greater abundance compared to longer dicarboxylic acids and ketoacids as well as the absence of the shorter chain acids is explained by this intramolecular abstraction mechanism. The absence of shorter chain products might also be decarboxylation reactions, *e.g.*, as in the case of 3-oxobutanoic acid, which is known to undergo thermal decarboxylation at temperatures as low as 50 °C.

The mechanism is somewhat different in the SG1, SG2, and SG3 materials containing dithiocarbamates.[14] The dithiocarbamates react rapidly with hydroperoxides as they are formed in photo-oxidizing polymer to give sulfuric acids which are catalysts for hydroperoxide decomposition and are themselves converted to iron and nickel sulfate. After the depletion of the metal thiolates, the rate of photo-oxidation reverts to that of the polymer containing the uncomplexed transition metal ion.

4. Conclusions

We propose that formation of ketoacids and dicarboxylic acids in photo- and thermo-oxidized degradable polyethylene is explained by a mechanism of intramolecular hydrogen abstraction via a cyclic transition state. This mechanism explains the large abundance of 4-oxopentanoic acid and butanedioic acid in comparison to the other ketoacids and dicarboxylic acids, because they are formed by an energetically more favorable six-membered transition state. Mono- and dicarboxylic acids were the dominating products in all the materials after both photo- and thermo-oxidation. Ketones, carboxylic acids and dicarboxylic acids were identified during the early stages of photo-oxidation, but only a few ketoacids were formed during the same period. The ketones disappeared in the most severely photo-oxidized films, while several ketoacids had been formed. The relative amount of dicarboxylic acids increased with prolonged photo-oxidation time.

A good correlation was found between the molecular weight decrease, the carbonyl index, and the amount of degradation products formed. Exceptions were the LDPE-MB films, in which fewer degradation products in smaller amounts were formed than in the other materials; this is mainly due to more cross-linking, which decreases the release of degradation products.

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