ERRATA

Thermal Degradation of Polyethylene in a Nitrogen Atmosphere of Low Oxygen Content. III. Structural Changes Occurring in Low-Density Polyethylene at Oxygen Contents Below 1.2%*

ARNE HOLMSTRÖM and ERLING SÖRVIK, *The Polymer Group, Department of Organic Chemistry, Chalmers University of Technology and University of Gothenburg, Fack, S-402 20 Göteborg, Sweden*

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Synopsis

Samples of low-density polyethylene, free from additives, were kept at temperatures between 284° and 355°C under nitrogen containing 1.16% oxygen or less. Changes in molecular weight distribution (MWD) and degree of long-chain branching (LCB) were followed by gel chromatography (GPC) and viscosity measurements. Other structural changes were investigated by infrared spectroscopy and differential scanning calorimetry (DSC). Both chain scission and molecular enlargement occur simultaneously. Chain scission accounts for the formation of low molecular weight material and volatiles. Molecular enlargement reactions cause an increase in LCB and ultimately the formation of insoluble material. At lower temperatures (284°C) an increase in the high molecular weight end of the MWD is observed. The amount of olefinic unsaturation, carbonyl, and ether groups increase with degradation. Conju-

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* In its original printing, this paper was unfortunately not in correct sequence. It is being republished here in its entirety.

gated systems are formed. The formation of thin discolored and insoluble surface layers indicate that the attack of oxygen is diffusion controlled. The DSC thermograms undergo large changes at 333° and 355°C, increasing with time and oxygen content. A reaction scheme for the thermo–oxidative degradation of polyethylene is discussed. Both inter- and intramolecular hydrogen abstractions by peroxy radicals are suggested to occur. Thus, the formation of *trans*-vinylene and ether groups results from intramolecular abstraction, while internal carbonyl groups are formed by intermolecular abstraction. Chain scission will be accomplished by both routes and together with "back-biting" is suggested to account for the formation of volatiles. The formation of conjugated sequences causing discoloration is correlated with the formation of *trans*-vinylene groups. Because of the restricted accessability of oxygen under our conditions, the reactions discussed previously for pure thermal degradation[1] are also considered to be important. The molecular enlargement observed is thus proposed to be mainly due to the combination of alkyl radicals even when oxygen is present.

INTRODUCTION

Processing polyethylene (PE) by extrusion and injection molding is carried out at increasingly higher temperatures. Today, a temperature of 350°C is not exceptional. In such processing equipment, PE is exposed not only to high temperature and shear forces, but also to the influence of oxygen. Little has been published on the structural changes in PE when subjected to such conditions.

Based on preliminary tests, Quackenbos[2] found that the oxidative attack during extrusion corresponds to a fairly low oxygen level. Thus, in his study on high-density polyethylene (HDPE), he treated the polymer in nitrogen containing 0.34% oxygen at temperatures between 150° and 400°C and measured the changes in intrinsic viscosity and carbonyl content.

In the first paper[3] in this series, we reported on thermal degradation of low-density polyethylene (LDPE) in the temperature range of 284–355°C and thermo-oxidative degradation at 355°C. The structural changes were followed by gel chromatography (GPC) and viscometry. The results obtained indicate that in addition to chain scission, molecular enlargement reactions play an important role in PE degradation. A major question in connection with these findings was whether the degree of long-chain branching (LCB) is changing or not. This was investigated in our next study concerning thermal degradation of LDPE in high-purity nitrogen (<0.0005% O_2) at 284° to 355°C.[1] Changes in molecular weight distribution (MWD), olefinic unsaturation, and crystalline melting behavior were also followed. In the present paper, a corresponding study is reported for thermo-oxidative degradation in 1.16% oxygen and less.

EXPERIMENTAL

Materials

The LDPE resin used, Unifos DFDS 6600, was kindly supplied by Unifos Kemi AB, Stenungsund, Sweden. It is a high-pressure product produced in a tubular reactor. Unifos has reported the LDPE to be free from addi-

tives. It has the following characteristics: density, 0.922 g/cm^3; melt index, 0.31 g/10 min; $[\eta]_{p\text{-xyl}}^{105°C} = 1.06$ dl/g; $\bar{M}_w = 97 \times 10^3$ (GPC); and $\bar{M}_n = 31 \times 10^3$ (GPC). Unifos DFDS 6600 is one of the polymers chosen for cooperative research work carried out under the auspices of Nordforsk.

A 0.25-mm-thick film from which samples were cut for the degradation experiments was molded at 130°C. The nitrogen–oxygen mixtures used in this study were delivered by AGA AB, Göteborg, Sweden and reported to contain 0.00028%, 0.020%, 0.041%, 0.105%, 0.340%, and 1.16% by volume of oxygen in nitrogen. (Note: One of the nitrogen–oxygen mixtures used previously[3] was reported by the manufacturer to contain 0.041% oxygen. Subsequent checks at AGA AB have proved the oxygen content to be 0.0095%. All other mixtures were found to contain the stated amounts of oxygen.)

Heat Treatment

The samples were heated as thin films placed on microscope cover glasses in a tubular oven 1.20 m long and 0.065 m in diameter. This construction made possible rapid heating and cooling of the sample and also controlling the temperature to better than ±1°C during the experiments. The heating temperatures were 284°, 315°, 333°, and 355°C; the heating times were 6, 12, 24, 48, 72, and 90 minutes at 333° and 355°C and 12, 24, 48, and 90 min at 284° and 315°C. The oven and the details of sample handling have been described previously.[3]

Gel Chromatography

A Waters Associates GPC Model 200, operating at 135°C with 1,2,4-trichlorobenzene as solvent, was used. The column combination consisted of five columns with permeabilities ranging from 10^3 to 10^7 Å, giving good separation in the molecular weight range of interest. For further experimental details, see reference 3.

To calculate the MWD, average molecular weights, and the degree of LCB from GPC and viscosity measurements, the computer program devised by Drott[4] was used. The degree of LCB is given as $\lambda = n_w/M$, where n_w is the weight-average number of trifunctional branch points per molecule. For further details and discussion, see reference 1. The calibration curve for linear PE was obtained via the universal calibration curve as described earlier.[3]

Viscosity Measurements

Measurements on intrinsic viscosity for LDPE were carried out in 1,2,4-trichlorobenzene at 135° ± 0.01°C and in p-xylene at 105° ± 0.01°C. Like Drott,[5] we found that both solvent systems gave the same result.

Ubbelohde dilution viscometers with flow times of pure solvent greater than 110 sec were used (capillary diameter 0.5 mm). In order to avoid problems caused by transferring hot solutions, the samples were dissolved

directly in the viscometers.   Viscosity determinations on the polystyrene standards were carried out in 1,2,4-trichlorobenzene at 135° ± 0.01°C.

Smooth curves were drawn to fit the experimental points, and curve values for the different heating times were used in the GPC data treatment.

Weight Measurements

The samples (~0.2 g) were weighed before and after heat treatment on a Mettler analytical balance.

Differential Scanning Calorimetry

A Perkin Elmer DSC-1 differential scanning calorimeter was used.   The heating rate was 8°C/min, the sample size was 10–12 mg, and the runs were performed in nitrogen atmosphere.   Before being analyzed, all samples were given the same thermal treatment, by being heated to 140°C and then cooled to room temperature in a controlled manner in the apparatus.

Infrared Analyses

All spectra were recorded on a Beckman infrared spectrophotometer, IR 9.   For the quantitative measurements of methyl contents, the ASTM D 2238-68 Method A was used.   The IUPAC HDPE NMWD[6] was utilized as a wedge material.   The calibration was then carried out on IUPAC LDPE B with a methyl content of 28.3 CH_3/1000 C.[6]   The other spectra were recorded directly on the films used in the degradation experiments.
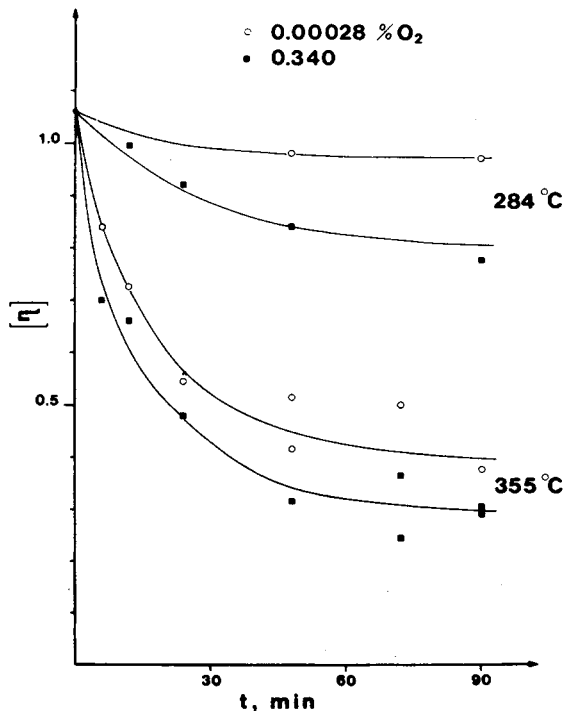

Fig. 1. Change in intrinsic viscosity as a function of heating time at 284° and 355°C.

RESULTS

For purposes of comparison, the results obtained previously in high-purity nitrogen[1] are occasionally included.

With several of the samples, a discolored surface layer was observed. Discoloration increased with time, temperature, and oxygen content. Heavily degraded samples were dark brown and contained a minor amount of insoluble material. For example, heating for 90 min at 355°C in 0.34% oxygen resulted in a thin brown surface layer and 2–3% insoluble polymer. Below this discrete layer, the polymer had turned yellow. The discoloration gradually decreased with the distance from the surface.

Intrinsic Viscosity, Molecular Weight Distribution, and Long-Chain Branching

Changes in intrinsic viscosity with time, temperature, and oxygen content are illustrated in Figure 1. Oxygen has a much larger relative effect on the decrease of $[\eta]$ at a lower temperature. No abrupt change in $[\eta]$ with oxygen content was observed.

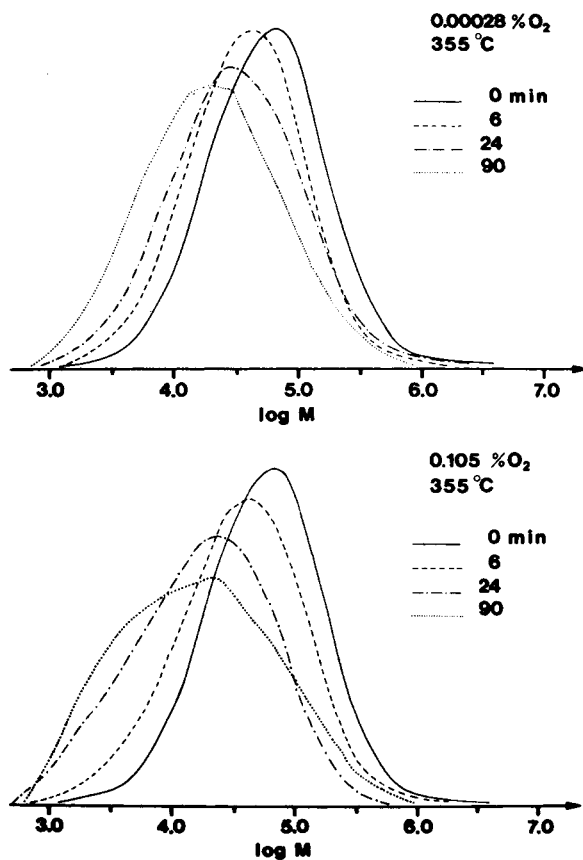In Figures 2–6, changes in MWD's as functions of time, temperature, and

Fig. 2. Change in MWD for samples heated at 355°C in 0.00028% and 0.105% oxygen.

oxygen content are illustrated. An increase in oxygen content results in a general shift of the MWD's toward lower molecular weights. As is shown in Figures 2 and 3, this will cause a pronounced increase in the amount of low molecular weight material. However, molecular enlargement will also occur. This is evidenced by complex changes of the high molecular weight tail of the MWD.

The effect of temperature on the changes in MWD at 0.105% oxygen is

TABLE I

Changes in Intrinsic Viscosity, $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ as a Function of Time, Temperature, and Oxygen Content

Temp., °C	Oxygen content, % O_2 in N_2	Time, min	$[\eta]_{,p\text{-xyl.}}^{105°C}$ dl/g	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
—	—	0	1.06	97	3.2
284	0.105	12	0.95	114	3.8
		24	0.92	114	4.5
		48	0.89	118	4.4
		90	0.86	107	4.7
	0.340	12	0.98	106	3.6
		24	0.91	113	4.2
		48	0.84	115	5.3
		90	0.81	117	6.7
	1.160	12	0.97	98	5.5
		24	0.91	95	5.0
		48	0.83	103	8.0
		90	0.76	115	9.4
315	0.105	12	0.88	111	4.5
		24	0.82	93	4.8
		48	0.76	87	5.7
		90	0.74	70	6.6
	0.340	12	0.88	96	4.3
		24	0.79	99	5.2
		48	0.73	87	7.3
		90	0.68	62	6.9
333	0.105	6	0.89	87	3.5
		12	0.79	89	4.4
		24	0.66	84	4.7
		48	0.58	97	7.3
		72	0.55	72	6.7
		90	0.54	65	5.8
	0.340	6	0.85	81	4.3
		12	0.72	85	5.4
		24	0.61	87	6.7
		48	0.56	79	7.8
		72	0.54	50	6.8
		90	0.54	53	7.2
	1.160	6	0.83	80	5.4
		12	0.71	95	6.9
		24	0.61	114	8.9
		48	0.54	85	9.7
		72	0.53	58	9.7
		90	0.52	56	10.1

TABLE I (*continued*)

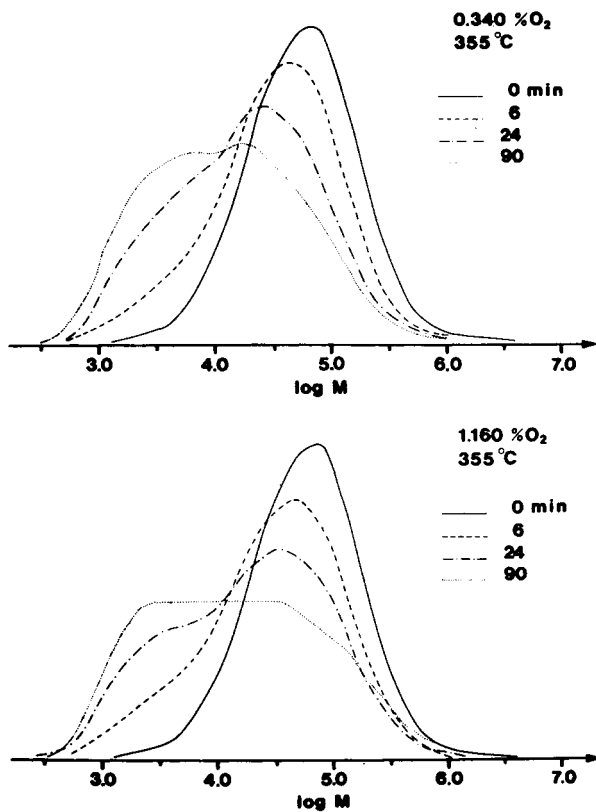| Temp., °C	Oxygen content, % O_2 in N_2	Time, min	$[\eta]_{,p\text{-xyl.}}^{105°C}$ dl/g	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
355	0.105	6	0.75	70	4.0
		12	0.64	54	4.4
		24	0.51	36	4.7
		48	0.38	42	5.6
		72	0.34	44	6.5
		90	0.33	44	6.6
	0.340	6	0.70	64	4.9
		12	0.60	42	5.2
		24	0.48	44	6.1
		72	0.31	35	7.2
		90	0.30	36	6.7
	1.160	6	0.70	62	6.0
		12	0.60	60	7.2
		24	0.49	50	8.3
		48	0.34	40	8.7
		72	0.27	42	10.4
		90	0.25	58	13.4

Fig. 3. Change in MWD for samples heated at 355°C in 0.340% and 1.16% oxygen.
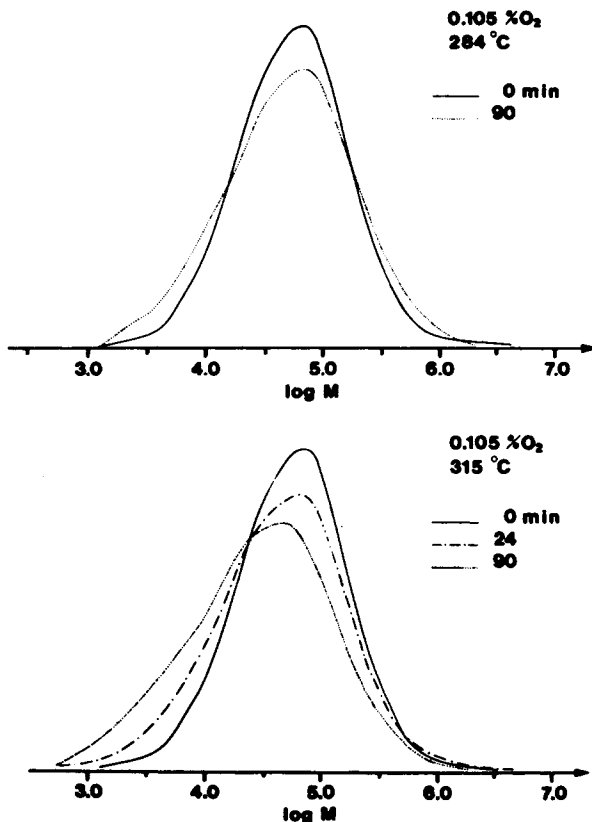
Fig. 4. Change in MWD for samples heated in 0.105% oxygen at 284° and 315°C.

illustrated in Figures 4 and 5. The formation of low molecular weight material rapidly increases with temperature. The high molecular weight end increases at 284°C. A decrease is noticed at higher temperatures. As is shown in Figure 6, the changes in MWD are more pronounced at higher oxygen contents.

The changes in MWD's shown above result in changes in molecular weight averages, given in Table I and illustrated in Figures 7 and 8. At 284°C the $\bar{M}_w$ values increase while at 315°C, 0.105% and 0.340% oxygen, a slight increase followed by an appreciable decrease is observed. At 355°C the $\bar{M}_w$'s show an initial rapid drop followed by minor changes. In 1.16% oxygen, an exceptional upward tendency is noticed after 90 min. $\bar{M}_w/\bar{M}_n$ values (Fig. 8) show a general increase with time and oxygen content.

Figures 9 and 10 show that the changes in the degree of LCB, λ, increase with temperature. At 284°C, a small increase is observed. At 315° and 333°C, the increase reaches a maximum. The maximum value is reached in a shorter time at higher oxygen levels. At 333°C and even more at 355°C and high oxygen levels, the relative rate of the changes is initially
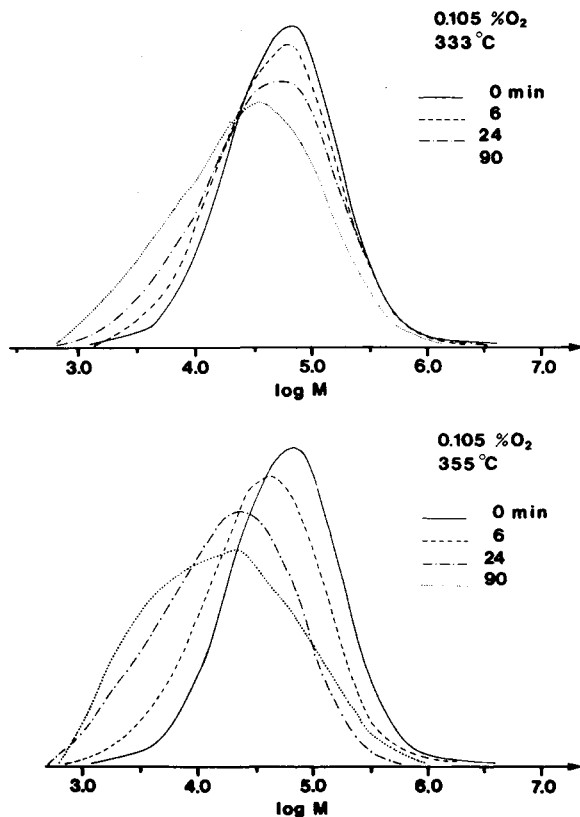
Fig. 5. Change in MWD for samples heated in 0.105% oxygen at 333° and 355°C.

remarkably small. At 355°C, no maximum value is observed. Instead, λ increases considerably after longer heating times.

Weight Loss

As shown in Figures 11 and 12, changes in sample weight are strongly influenced by both temperature and oxygen content. At 284°C and 0.34% oxygen, a slight increase in weight is observed. In all other cases, weight loss occurs.

Infrared Analyses

The results of IR analyses of unsaturated groups are shown in Figures 13–16. All films were of the same thickness, 0.25 mm. The peak positions were: carbonyl, 1720 cm^{-1}; vinylidene, 890 cm^{-1}; vinyl, 910 cm^{-1}; and *trans*-vinylene, 970 cm^{-1}.

To investigate the nature of the carbonyl groups, a method developed by Cooper and Prober[7] was followed. A sample heated at 355°C for 90 min in 0.340% oxygen was immersed in 0.2M NaOH in 95% ethanol and ana-
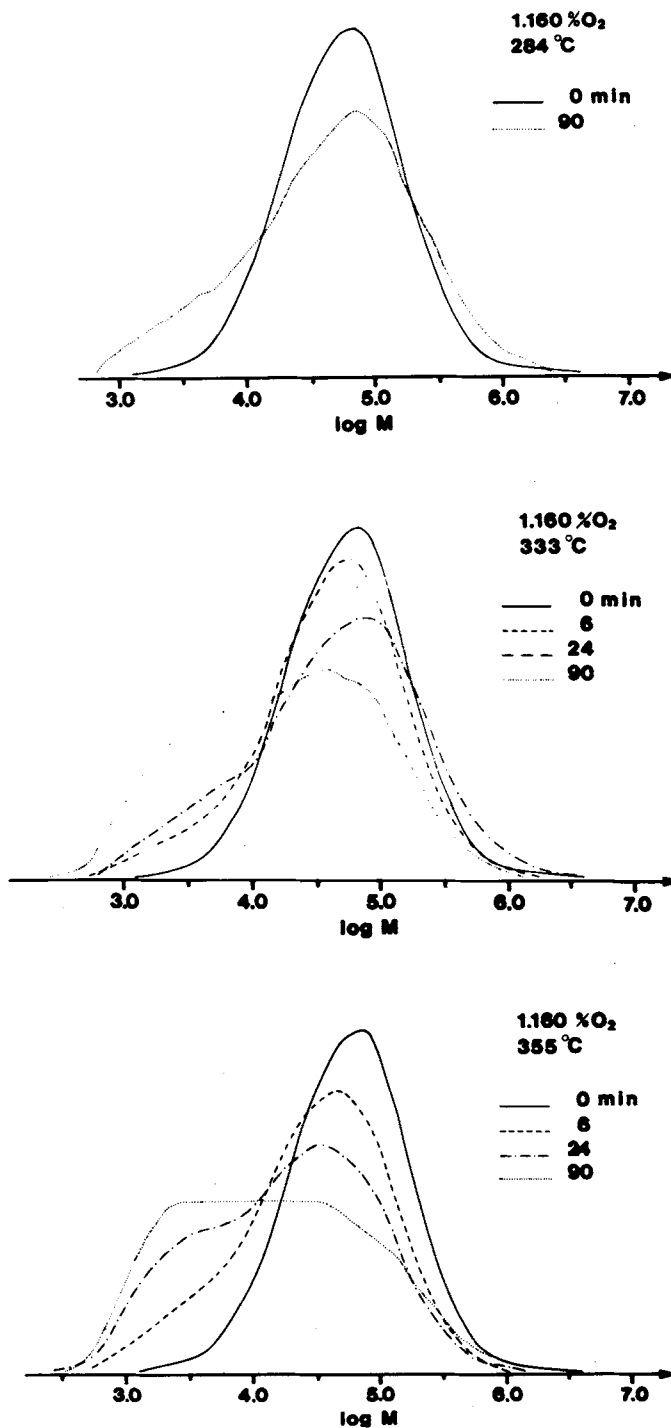
Fig. 6. Change in MWD for samples heated in 1.16% oxygen at 284°, 333°, and 355°C.
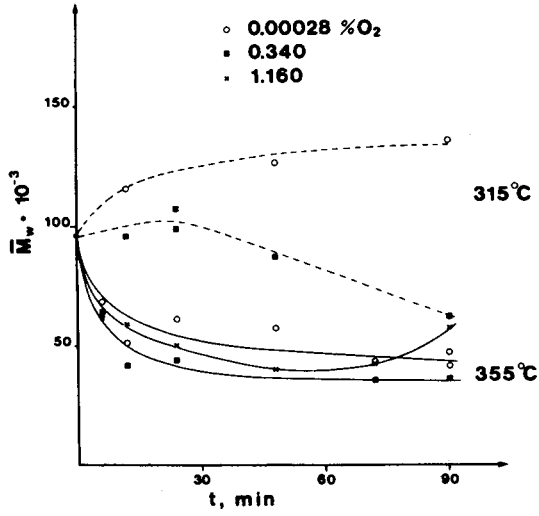
Fig. 7. Change in $\bar{M}_w$ as a function of heating time at 315° and 355°C.
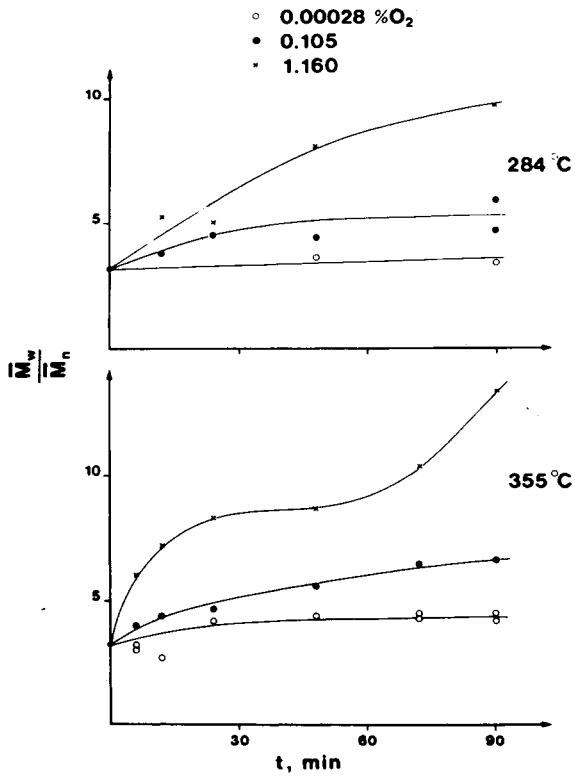

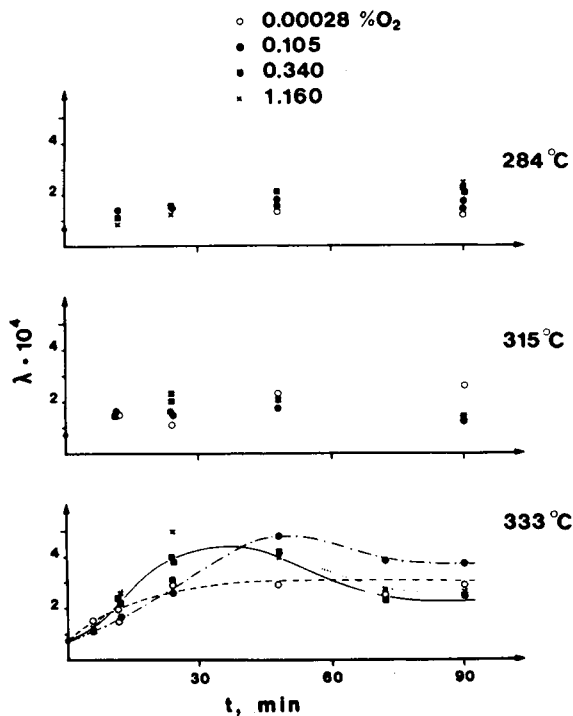Fig. 8. Change in $\bar{M}_w/\bar{M}_n$ as a function of heating time at 284° and 355°C.

Fig. 9. Change in degree of LCB (λ) as a function of heating time at 284°, 315°, and 333°C.
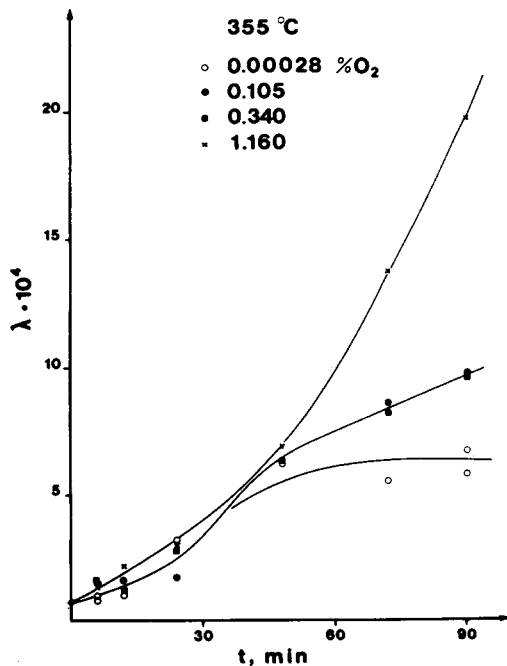

Fig. 10. Change in degree of LCB (λ) as a function of heating time at 355°C.
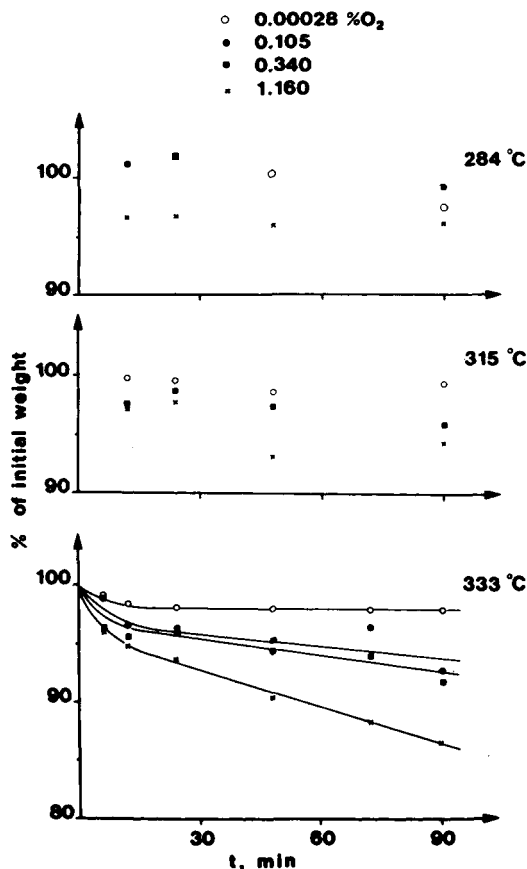
Fig. 11. Weight changes at 284°, 315°, and 333°C.

lyzed several times during 90 days. No changes in the carbonyl peak were observed and no peak appeared at 1585 cm^{-1}, indicating that no carboxylic groups were present.

The effect of temperature on carbonyl content is negligible at 0.105% oxygen (Fig. 13) and is only slightly larger at higher oxygen contents. At all temperature levels, however, the effect of the oxygen content is pronounced (Fig. 14).

Olefinic unsaturation increases with time, temperature, and oxygen content. Figure 15 illustrates the effect of heating time. The vinyl and trans-vinylene groups show a larger relative increase than the vinylidene groups. Increasing the oxygen content at 355°C results in a large increase in trans-vinylene groups compared to vinyl and vinylidene groups (Fig. 16). Results from the other heating temperatures show that the content of trans-vinylene groups is strongly affected both by temperature and oxygen content. On the other hand, the content of vinyl and vinylidene groups is very sensitive to temperature changes, but only slightly affected by changes in oxygen content.
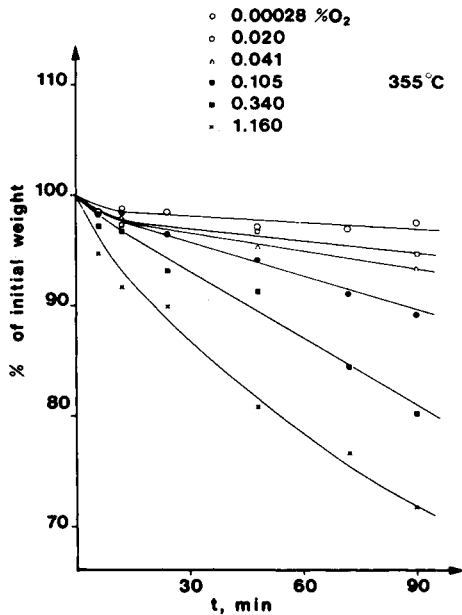
Fig. 12. Weight changes at 355°C.

Fig. 13. Change in infrared spectra in the range of 1600–1800 cm⁻¹ for samples heated at 284° and 355°C in 0.105% oxygen.
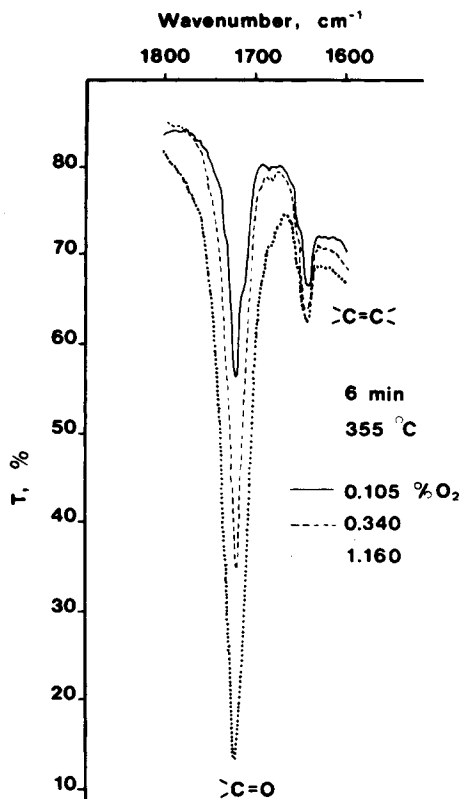
Wavenumber, cm⁻¹

1800   1700   1600

80

70

$>C=C<$

60

6 min

50   355 °C

—— 0.105 % O_2

40   ---- 0.340

1.160

30

20

T, %

10    $>C=O$

Fig. 14. Change in infrared spectra in the range of 1600–1800 cm⁻¹ for samples heated
for 6 min at 355°C.

Wavenumber, cm⁻¹

1000 900 800   1000 900 800   1000 900 800   1000 900 800

80

70

R-CH=CH-R'

60    $\begin{matrix} R' \\ R \end{matrix} C=CH_2$

50

R-CH=CH₂

T, %

Original sample

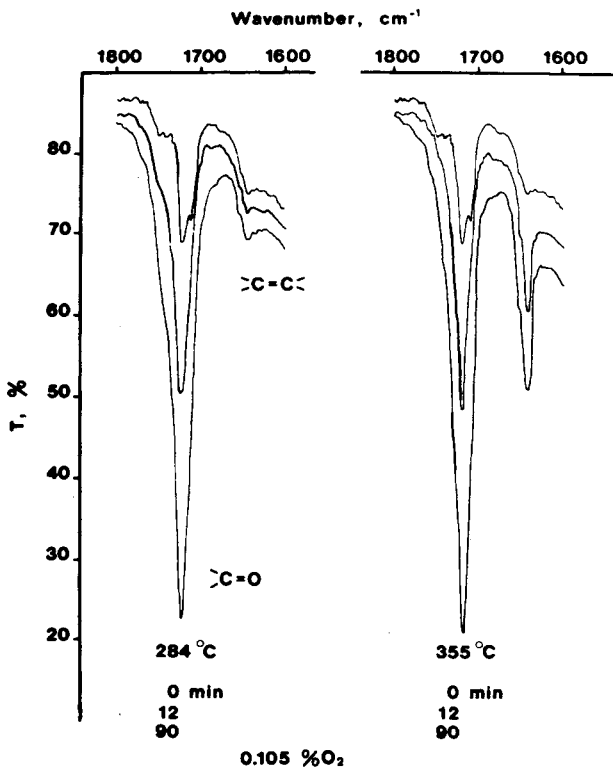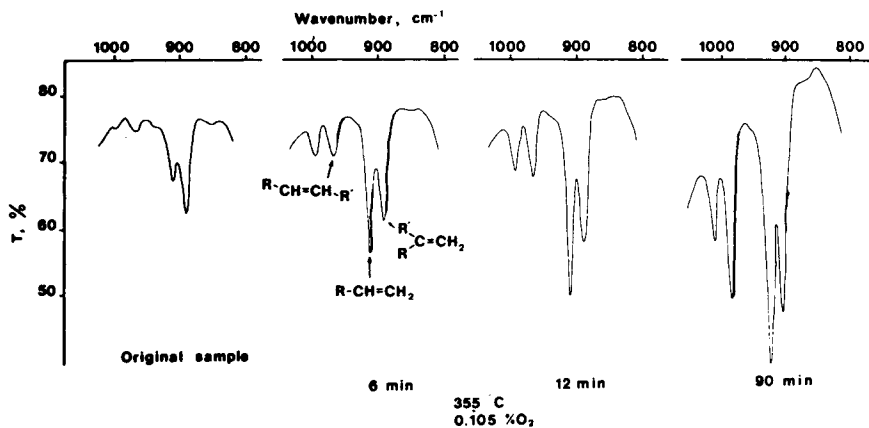6 min   12 min   90 min

355 °C
0.105 %O₂

Fig. 15. Change in infrared spectra in the range of 800–1000 cm⁻¹ for samples heated
at 355°C in 0.105% oxygen.
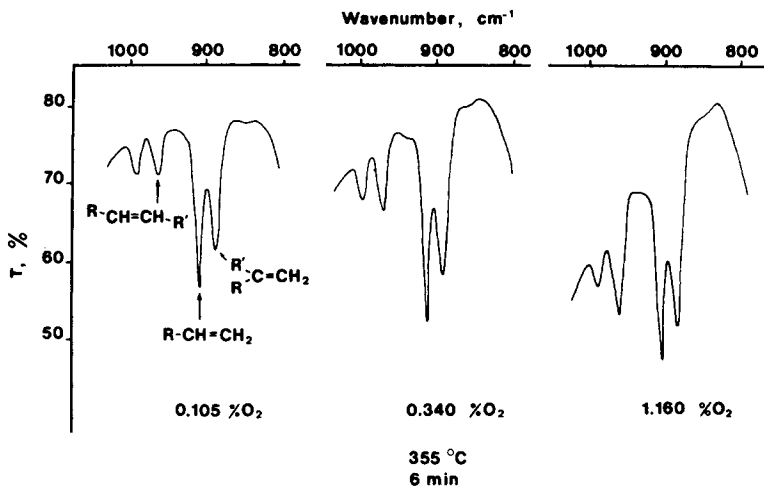
Fig. 16. Change in infrared spectra in the range of 800–1000 cm^{-1} for samples heated for 6 min at 355°C.

Besides an increase in unsaturation, ether groups also increase with time, temperature, and oxygen content. No hydroxylic groups were formed, however. The broad ether band is centered at 1080 cm^{-1}. At this position, there is initially a small peak usually assigned to C–C stretching.[8] Since the amount of C–C is approximately constant, we ascribe the large increase observed in this region to ether groups.

The methyl contents in samples heated at 355° and 333°C are given in Table II. At low oxygen levels there is an indication of a slight increase in the methyl content after 6 and 24 min of heating. At higher oxygen levels and short heating times, no increase is observed. Samples treated in 0.00028% and 0.105% oxygen for a long time show a considerable decrease in methyl content. Such a decrease is followed by an increase at the highest oxygen level.

Differential Scanning Calorimetry

The DSC thermograms for samples heated at 355°C in 1.16% oxygen are shown in Figure 17. Samples heated for 6 min show a change in peak temperature from 384° to 387°K. After 24 min, another peak develops at 384°K. Further heating results in the formation of still another peak at 380°K, the disappearance of the peak at 387°K, and a reduction of the peak at 384°K. The thermogram area per unit weight is constant up to 24 min of heating and is then reduced to about 60% of the original after 90 min. The rate of change decreases with decreasing heating temperature and oxygen content, being negligible at 315° and 284°C.

DISCUSSION

The formation of thin, highly discolored surface layers proves that, under the conditions used, the attack of oxygen is diffusion controlled. Restric-

TABLE II
Methyl Content as a Function of Time, Temperature, and Oxygen Content

| Temp., °C | Oxygen content, % O₂ in N₂ | Time, min | Methyl content, CH₃/1000 C | |
			Uncorrected	Correcteda
—	—	0	21	20
333	0.340	6	20	19
		24	21	19
		90	23	21
355	0.00028	6	24	22.5
		24	24	22.5
		90	17	15
	0.105	6	22	21
		24	24	22
		90	17	14.5
	0.340	6	21	19.5
		24	20	17.5
	1.160	6	21	19.5
		24	22	19.5
		48	20	16.5
		90	23	19

a Correction has been made for CH₃ groups at the main chain ends.   For discussion of the correction, see text.
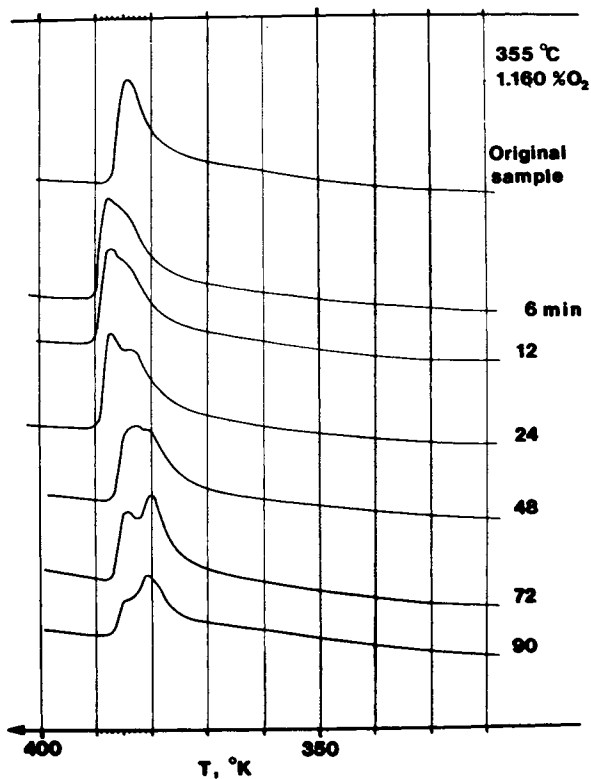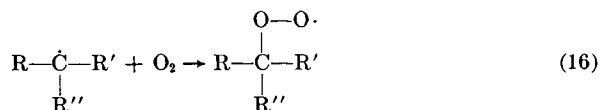

Fig. 17. DSC thermograms for samples heated at 355°C in 1.16% oxygen.

tion of the direct oxygen attack to the surface layer does not preclude the possibility that degraded polymer chains diffuse into the molten polymer mass, however.   In this way the observed gradient in discoloration may be formed.   Thus, since the treated samples are heterogeneous in composition, the determinations must be considered as qualitative.   Even a considerable reduction of sample thickness would not ensure a homogeneously oxidized material.[9]   Furthermore, a reduction of sample thickness would lead to a sample size insufficient for the necessary characterization.

Degradation Reaction Mechanisms

Because of the restricted accessability of oxygen, both thermal and thermo-oxidative degradation mechanisms must be taken into account when interpreting our data.   Mechanisms discussed for thermal degradation in our previous paper[1] are summarized in Figure 18.

The following designations are used: R, R' = alkyl groups; R'' = hydrogen or alkyl group; $R'''\cdot$ = alkyl radical, $RO\cdot$, $ROO\cdot$, $HO\cdot$, or $HO_2\cdot$.   The initiation reactions (1)–(3) in Figure 18 are the most probable starting reactions even when oxygen is present.   The oxygen available will immediately attack the radicals formed according to reaction (16):

$$R\!-\!\overset{\displaystyle R''}{\underset{\displaystyle R''}{\overset{|}{\underset{|}{C}}}}\!-\!R' + O_2 \rightarrow R\!-\!\overset{\displaystyle O\!-\!O\cdot}{\underset{\displaystyle R''}{\overset{|}{\underset{|}{C}}}}\!-\!R' \tag{16}$$

where $E_a \approx 0$ kcal/mole.[10]

Hydroperoxides will then be formed by inter- or intramolecular hydrogen abstraction.

Intermolecular hydrogen abstraction, reaction (17), followed by reactions (18)–(21) will result in aldehydes, ketones, or hydroxy compounds:

$$R\!-\!\overset{\displaystyle O\!-\!O\cdot}{\underset{\displaystyle R''}{\overset{|}{\underset{|}{C}}}}\!-\!R' + R_a\!-\!\overset{\displaystyle}{\underset{\displaystyle R''_a}{\overset{|}{\underset{|}{C}H}}}\!-\!R'_a \rightarrow R\!-\!\overset{\displaystyle O\!-\!OH}{\underset{\displaystyle R''}{\overset{|}{\underset{|}{C}}}}\!-\!R' + R_a\!-\!\overset{\displaystyle}{\underset{\displaystyle R''_a}{\overset{|}{\underset{|}{\dot{C}}}}}\!-\!R'_a \tag{17}$$
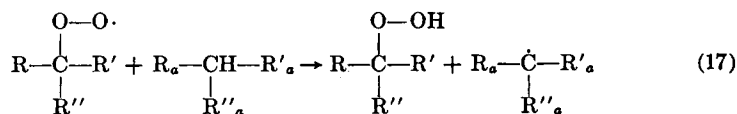
where $E_a \approx 10.5$ kcal/mole;[10]

$$R\!-\!\overset{\displaystyle O\!-\!OH}{\underset{\displaystyle R''}{\overset{|}{\underset{|}{C}}}}\!-\!R' \rightarrow R\!-\!\overset{\displaystyle O\cdot}{\underset{\displaystyle R''}{\overset{|}{\underset{|}{C}}}}\!-\!R' + \cdot OH \tag{18}$$

where $E_a \approx 44$ kcal/mole[11];

$$R\!-\!\overset{\displaystyle O\cdot}{\underset{\displaystyle R''}{\overset{|}{\underset{|}{C}}}}\!-\!R' \rightarrow R\!-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!R'' + R'\cdot \tag{19}$$

Initiation

$$R\text{-}CH_2\text{-}\underset{\overset{|}{C}H_2}{C}\text{-}CH_2\text{-}R' \longrightarrow R\cdot\cdot\cdot CH_2\text{-}\underset{\overset{|}{C}H_2}{C}\text{-}CH_2\text{-}R' \qquad \textbf{1}$$

$$R\text{-}CH_2\text{-}CH\text{=}CH_2 \longrightarrow R\cdot\cdot\cdot CH_2\text{-}CH\text{=}CH_2 \qquad \textbf{2}$$

$$R\text{-}CH_2\text{-}CH\text{=}CH\text{-}R' \longrightarrow R\cdot\cdot\cdot CH_2\text{-}CH\text{=}CH\text{-}R' \qquad \textbf{3}$$
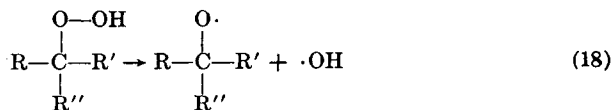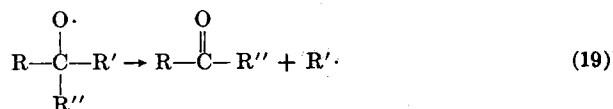
Propagation

Depolymerization
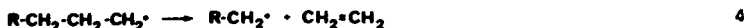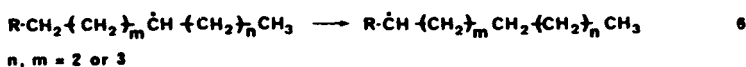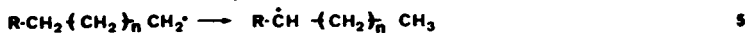
$$R\text{-}CH_2\text{-}CH_2\text{-}CH_2\cdot \longrightarrow R\text{-}CH_2\cdot \ + \ CH_2\text{=}CH_2 \qquad \textbf{4}$$

Intramolecular hydrogen abstraction

$$R\text{-}CH_2\text{-}(CH_2)_n CH_2\cdot \longrightarrow R\text{-}\dot{C}H\text{-}(CH_2)_n CH_3 \qquad \textbf{5}$$

$$R\text{-}CH_2\text{-}(CH_2)_m \dot{C}H\text{-}(CH_2)_n CH_3 \longrightarrow R\text{-}\dot{C}H\text{-}(CH_2)_m CH_2\text{-}(CH_2)_n CH_3 \qquad \textbf{6}$$

n, m = 2 or 3

Subsequent β-scission

$$R\text{-}CH_2\text{-}\dot{C}H\text{-}(CH_2)_p CH_3 \left\langle \begin{array}{l} R\cdot\cdot CH_2\text{=}CH\text{-}(CH_2)_{\overline{p}} CH_3 \qquad \textbf{7} \\[2mm] R\text{-}CH_2\text{-}CH\text{=}CH_2\cdot \ \ \cdot CH_2\text{-}(CH_2)_{\overline{p\text{-}2}} CH_3 \qquad \textbf{8} \end{array} \right.$$

Intermolecular hydrogen abstraction

$$R\text{-}CH_2\cdot \ \cdot R\text{-}\underset{}{\overset{R''}{\dot{C}}H}\text{-}CH_2\text{-}R' \longrightarrow R\text{-}CH_3 \cdot \ R\text{-}\underset{}{\overset{R''}{\dot{C}}}\text{-}CH_2\text{-}R' \qquad \textbf{9}$$

Subsequent β-scission

$$R\text{-}\dot{C}H\text{-}CH_2\text{-}R' \longrightarrow R\text{-}CH\text{=}CH_2 \ \cdot \ \cdot R' \qquad \textbf{10 a}$$

$$R\text{-}CH_2\text{-}\underset{\overset{|}{\underset{R''}{C}H_2}}{\dot{C}}\text{-}CH_2\text{-}R' \longrightarrow R\text{-}CH_2\text{-}\underset{\overset{|}{C}H_2}{C}\text{=}CH_2\text{-}R' \ \cdot \ \cdot R'' \qquad \textbf{10 b}$$

$$R\text{-}CH_2\text{-}\underset{\overset{|}{\underset{R''}{C}H_2}}{CH}\text{-}\dot{C}H\text{-}R' \longrightarrow R\text{-}CH_2\text{-}CH\text{=}CH\text{-}R' \ \cdot \ \cdot CH_2\text{-}R'' \qquad \textbf{10 c}$$
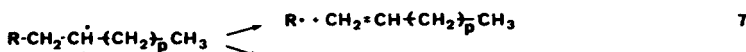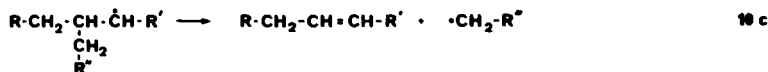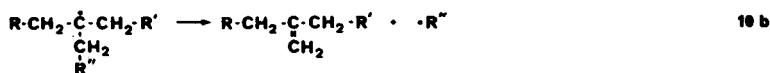
Isomerization of vinyl group

$$R\cdot \ \cdot R'\text{-}CH_2\text{-}CH\text{=}CH_2 \longrightarrow R\text{-}H \ \cdot \ R'\text{-}\dot{C}H\text{-}CH\text{=}CH_2 \qquad \textbf{11}$$

$$\downarrow$$

$$R'\text{-}CH\text{=}CH\text{-}CH_3 \cdot R\dot{:} \ \xleftarrow{\ R\dot{-}H\ } \ R'\text{-}CH\text{=}CH\text{-}CH_2\cdot$$
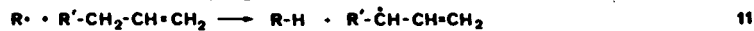
Termination

Combination

$$R\text{-}CH_2\cdot \ \cdot \cdot CH_2\text{-}R' \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}R' \qquad \textbf{12}$$

$$R\text{-}CH_2\cdot \ \cdot R\text{-}\dot{C}H\text{-}R'' \longrightarrow R\text{-}CH_2\text{-}\underset{\overset{|}{R'}}{C}H\text{-}R'' \qquad \textbf{13}$$

Disproportionation

$$R\text{-}CH_2\text{-}CH_2\cdot \ \cdot \cdot CH_2\text{-}R' \longrightarrow R\text{-}CH\text{=}CH_2 \ \cdot \ R\text{-}CH_3 \qquad \textbf{14}$$

$$R\text{-}CH_2\cdot \ \cdot R'\text{-}\dot{C}H\text{-}CH_2\text{-}R'' \longrightarrow R\text{-}CH_3 \ \cdot \ R'\text{-}CH\text{=}CH\text{-}R'' \qquad \textbf{15}$$

Fig. 18. Reaction scheme[1] for pure thermal degradation of polyethylene.

$$R-\overset{\underset{\displaystyle R''}{|}}{\overset{\overset{\displaystyle O\cdot}{|}}{C}}-R' + R_aH \rightarrow R-\overset{\underset{\displaystyle R''}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-R' + R_a\cdot \tag{20}$$
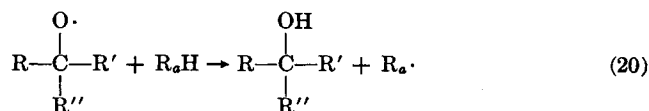
where $E_a \approx 3\text{--}11$ kcal/mole[10] for reaction (20); and

$$R-CH_2-\overset{\overset{\displaystyle H}{\diagup}}{CH}\overset{\displaystyle O}{\underset{\underset{\displaystyle CH_2}{\diagdown\diagup}}{\underset{\displaystyle CH_2\quad CR'R''}{|\quad\quad|}}} \quad \longrightarrow \quad R-CH_2-\overset{.}{C}H-CH_2-CH_2-\overset{\underset{\displaystyle R''}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-R' \tag{21}$$
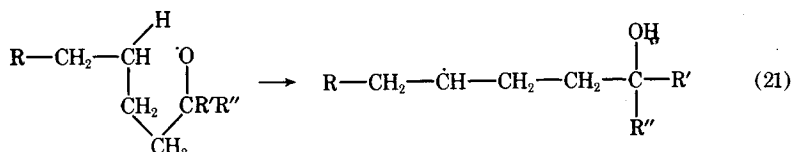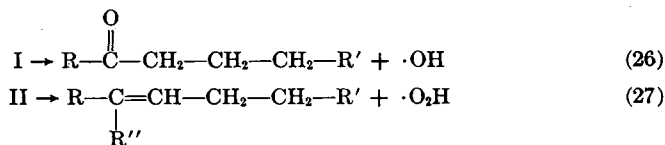
Due to their labile hydrogen, aldehydes formed are considered to undergo rapid hydrogen abstraction and subsequent carbon monoxide loss under the prevailing conditions.
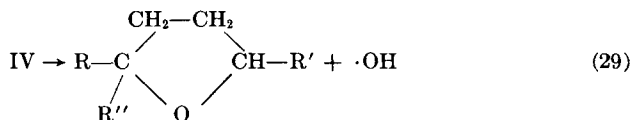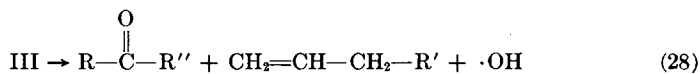
The most likely intramolecular hydrogen abstractions are given[10] in reactions (22)–(25):

$$R-\overset{\underset{\displaystyle \cdot}{|}}{\overset{\overset{\displaystyle O-OH}{|}}{C}}-CH_2-CH_2-CH_2-R' \quad (I) \tag{22}$$

$$R-\overset{\underset{\displaystyle R''}{|}}{\overset{\overset{\displaystyle O-OH}{|}}{C}}-\overset{.}{C}H-CH_2-CH_2-R' \quad (II) \tag{23}$$

$$R-\overset{\overset{\displaystyle O-O\cdot}{|}}{\underset{\underset{\displaystyle R''}{|}}{C}}-CH_2-CH_2-R'$$

$$R-\overset{\underset{\displaystyle R''}{|}}{\overset{\overset{\displaystyle O-OH}{|}}{C}}-CH_2-\overset{.}{C}H-CH_2-R' \quad (III) \tag{24}$$

$$R-\overset{\underset{\displaystyle R''}{|}}{\overset{\overset{\displaystyle O-OH}{|}}{C}}-CH_2-CH_2-\overset{.}{C}H-R' \quad (IV) \tag{25}$$
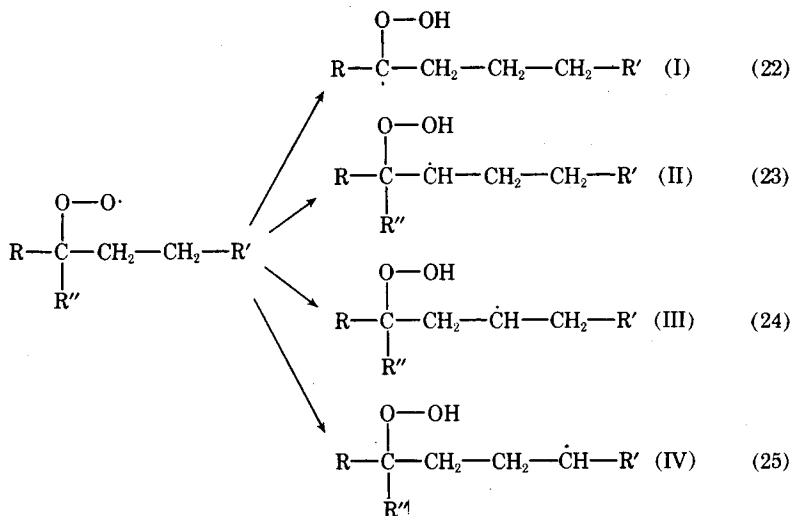
Reaction (22), $E_a \approx 37$ kcal/mole,[10] implies a four-membered ring transition state. It is thus less favored than reactions (23)–(25), $E_a \approx 17, 11,$ and 17 kcal/mole,[10] requiring five-, six-, and seven-membered rings, respectively.

The most probable subsequent reactions[10] will result in the formation of aldehydes, ketones, tetrahydrofuran derivatives (THF derivatives), and vinyl and vinylene groups, reactions (26)–(29):

$$I \rightarrow R-\overset{\overset{\displaystyle O}{\parallel}}{C}-CH_2-CH_2-CH_2-R' + \cdot OH \tag{26}$$

$$II \rightarrow R-\overset{\underset{\displaystyle R''}{|}}{C}=CH-CH_2-CH_2-R' + \cdot O_2H \tag{27}$$

$$\text{III} \rightarrow R\overset{\overset{\displaystyle O}{\|}}{-C}-R'' + CH_2{=}CH{-}CH_2{-}R' + \cdot OH \tag{28}$$

$$\text{IV} \rightarrow R{-}C\overset{\displaystyle CH_2{-}CH_2}{\underset{\displaystyle R''}{\diagup\diagdown}}\overset{}{\underset{\displaystyle O}{\diagdown\diagup}}CH{-}R' + \cdot OH \tag{29}$$
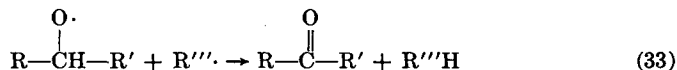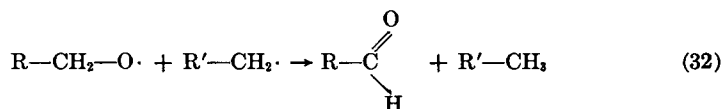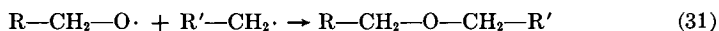
In combination with reaction (30), the oxygen-induced doubling of the radical concentration in each intermolecular reaction sequence (reactions (17) and (18)) will result in the well-known "auto-oxidation":

$$R{-}\underset{\displaystyle R''}{\overset{|}{C}H}{-}R' + \cdot R''' \rightarrow R{-}\underset{\displaystyle R''}{\overset{|}{\dot{C}}}{-}R' + R'''H \tag{30}$$
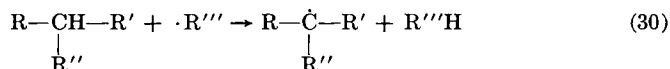
If $\cdot R''' = \cdot OH, E_a \approx 1\text{--}2\,\text{kcal/mole}$.[10]

The termination reactions, involving alkoxy radicals considered to be of importance in the thermo-oxidative degradation of PE under our conditions, are reactions (31)–(33):

$$R{-}CH_2{-}O\cdot + R'{-}CH_2\cdot \rightarrow R{-}CH_2{-}O{-}CH_2{-}R' \tag{31}$$

$$R{-}CH_2{-}O\cdot + R'{-}CH_2\cdot \rightarrow R{-}C\overset{\displaystyle O}{\underset{\displaystyle H}{\diagup\diagdown}} + R'{-}CH_3 \tag{32}$$

$$R{-}\underset{\displaystyle }{\overset{\displaystyle O\cdot}{\overset{|}{C}}}H{-}R' + R'''\cdot \rightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R' + R'''H \tag{33}$$

Disproportionation, reactions (32) and (33), must be considered most probable at the temperatures used.

The Effect of Oxygen

In pure thermal degradation of PE, chain scission and molecular enlargement reactions compete with the latter reactions dominating at 315°C and below.[1] Introduction of oxygen in the degradation system will cause the chain scission reactions to increase drastically as evidenced by a high weight loss (Fig. 12) and an appreciable increase in the low molecular weight end of the MWD's (Figs. 2 and 3). However, even in the presence of oxygen, molecular enlargement will occur. The complex changes in the high molecular weight tail of the MWD's even in 1.16% oxygen (Fig. 6), the increase in LCB (Fig. 10), and the presence of insoluble material are all results of such reactions. Other significant effects of oxygen are the formation of substantial amounts of carbonyl and *trans*-vinylene groups and the formation of conjugated systems, evidenced by discoloration.

The mechanisms suggested above for the thermo-oxidative degradation of PE indicate that the introduction of oxygen gives rise to both greatly increased radical concentration and the formation of small, mobile, reactive radicals like $\cdot OH$ and $\cdot O_2H$. Since there is a general shortage of oxygen under our conditions, it is unlikely that it can add to all alkyl radi-

cals formed, reaction (16). Therefore, reactions of the pure thermal type (Fig. 18) will also increase and play an important role in the thermo-oxidative degradation.

Molecular Enlargement

Although molecular enlargement also occurs at high temperatures and oxygen levels (see Fig. 6), it is likely that the formation of LCB, cross-linked structures, and chain elongation is due mainly to a combination of alkyl radicals, reactions (12) and (13) in Figure 18, while alkoxy radicals mainly undergo disproportionation, reactions (32) and (33). However, primary alkoxy radicals may undergo combination to some extent according to reaction (31). The large increase in ether content observed is not mainly due to this reaction but to reaction (29), as will be discussed below.

The increase observed in LCB, Figures 9 and 10, is supposed to be due to the increase in internal unsaturation and other structural anomalies which are prone to give stabilized secondary radicals liable to undergo reaction (13) in Figure 18. The decrease in LCB after the maximum at 315° and 333°C might be explained by crosslinking, giving insoluble material or chain scission of the branched molecules. On the other hand, chain scission of crosslinked material will increase the content of soluble long-chain branched material. This might explain the large increase in LCB at 355°C, 1.16% oxygen, (Fig. 10).
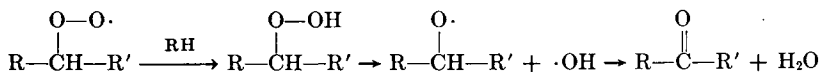
Discoloration

The formation of discolored material is difficult to explain. No investigations concerning the mechanism have been published. According to our results, the prerequisite for color formation is the presence of oxygen and substantial structural changes. No discoloration is observed if LDPE is heated in nitrogen[1] or degraded in a vacuum down to a mobile liquid.[12] In thermo-oxidative degradation, discoloration increases with time, temperature, and oxygen content in the same general way as crosslinking and formation of volatiles.

Thermal degradation of LDPE results in a substantial increase in vinyl and vinylidene groups irrespective of oxygen content. However, only in the presence of oxygen does a substantial increase in carbonyl and trans-vinylene groups occur (Figs. 14 and 16). The temperature at which the thermo-oxidative degradation is carried out plays an important role when structural changes and color formation are concerned. Heating LDPE in air at 180°C for 30 min results in a large increase in carbonyl content, but no additional olefinic unsaturation and no discoloration.[13] Heating at 284°C in 1.16% oxygen to about the same carbonyl content (~90 min) results in discoloration. At the same time, an appreciable amount of trans-vinylene groups is formed.

It is well known that in aliphatic compounds, five to seven conjugated unsaturated bonds are required to obtain absorption within the visible sprectral range.[14] Carbonyl and olefinic groups are approximately equal in their increment of the wavelength of the absorption maxima.

From a mechanistic point of view, the way of formation of conjugated systems large enough to result in discoloration is the main problem to be solved. Grassie[15] and Mayo[16] both consider formation of internal carbonyl groups to proceed according to reactions (17), (18), and (33) involving intermolecular hydrogen abstraction:

$$O—O\cdot \qquad\qquad O—OH \qquad O\cdot \qquad\qquad\qquad O$$
$$R—\overset{|}{C}H—R' \xrightarrow{RH} R—\overset{|}{C}H—R' \rightarrow R—\overset{|}{C}H—R' + \cdot OH \rightarrow R—\overset{\|}{C}—R' + H_2O$$

Intramolecular hydrogen abstraction by the peroxy radical will result in vinylene, reactions (23) and (27); THF derivatives, reactions (25) and (29); and vinyl groups by chain scission, reactions (24) and (28).

Fish[10] has shown that the intramolecular hydrogen abstraction will gradually increase with temperature. At ambient temperature, such reactions are not significant compared to the intermolecular hydrogen abstraction, but at 325°C they will dominate. This temperature dependence may explain why no formation of vinylene unsaturation is observed although carbonyl groups increased greatly when PE was heated for 30 min at 180°C in air.

Formation of conjugated sequences may proceed either by a "zipper" type of reaction or by a cumulation of random reactions. The presence of internal olefinic unsaturation or carbonyl groups should *per se* favor a "zipper" type of reaction via allylic activation of hydrogen abstraction.

Based on E_a values, formation of THF derivatives should be as likely as formation of vinylene unsaturation, while chain scission should be more strongly favored. Formation of conjugated systems should thus be very unlikely. It has been reported, however, that 25–55% THF derivatives were obtained when alkanes were oxidized under oxygen deficient conditions at about 300°C.[10] Formation of vinylene unsaturation during the thermo-oxidative degradation of PE might thus be more favored than could be expected from the E_a values reported for alkanes. In any case, the probability of formation of conjugated systems containing more than five double bonds should be low. This is in accordance with the fact that color formation is observed only after substantial structural changes.

As neither hydroxylic nor carboxylic groups are present, the observed increase in ether groups is supposed to be due to the formation of THF derivatives according to reactions (25) and (29). This is confirmed by the fact that the ether band in the IR spectrum appears at the same wavenumber as for THF derivatives in general.

Chain Scission and Weight Loss

As shown in Figures 11 and 12, the weight loss increases greatly with oxygen content except at 284°C, 0.340% oxygen, where a slight increase in weight is observed. This increase may be due to the fact that more oxygen is incorporated in the polymer, e.g., as carbonyl groups, cf. Figure 13, than the weight of the volatiles formed.

The presence of oxygen will cause a considerable increase in the radical

concentration, since every oxygen molecule that reacts with an alkyl radical and undergoes intermolecular hydrogen abstraction will result in two radicals, one of which is mainly the mobile and highly reactive ·OH. Due to the low specificity of the hydrogen abstraction by ·OH,[10] a random attack on the polymer chains may occur to a considerable extent, reaction (30). If oxygen is not readily available, chain rupture is accomplished by β-scission, reaction (10) in Figure 18. If the radical adds oxygen, the most likely intramolecular hydrogen abstraction, reaction (24), will also result in chain scission. The rapid increase in low molecular weight material with increasing oxygen content, Figures 2–6, is suggested to be due mainly to these chain scission reactions. Another reaction that also may contribute to the observed chain scission is β-scission of a secondary or tertiary alkoxy radical, reaction (19).

As can be seen from the MWD's, material with molecular weight in the order of 500 is often formed. At the temperatures used, such material will volatilize. Contrary to what could be expected for pure thermal degradation,[1] it is thus likely that random chain scission contributes to the formation of volatiles in thermo-oxidative degradation.

As discussed in the previous paper,[1] the formation of volatiles by intramolecular hydrogen abstraction (back-biting) of alkyl radicals and subsequent β-scission, Figure 18, reactions (5), (6), (7), and (8), is considered to be most important for the pure thermal degradation of PE. In thermo-oxidative degradation, primary alkyl radicals can be directly formed in reaction (19), and will also easily be generated through hydrogen abstraction and subsequent carbon monoxide loss from the aldehyde formed in reaction (19) or in reaction (28). If oxygen is not readily available, these primary radicals will easily form volatiles by back-biting as in pure thermal degradation. This back-biting may also be repeated. On the other hand, if the primary radical adds oxygen, back-biting according to reaction (24), with R = R″ = H, will only be possible once, since a vinyl group will terminate the polymer chain. Another possible back-biting exists, however, if an alkoxy radical undergoes reaction (21), parallel to the behavior of an alkyl radical, and results in volatiles by subsequent β-scission. A new primary polymer alkyl radical may also be generated.

Due to the low oxygen levels, the contribution to the volatile material from back-biting by alkyl radicals is considered to be important for the thermo-oxidative degradation of PE also.

DSC Thermograms

Pyrolytic gas-chromatographic studies of PE at temperatures above 450°C have shown that branches are split off.[17] Such scission will result in vinylidene groups, Figure 18, reaction (10b).

Our measurements show that the content of vinylidene groups increases during degradation, Figure 15. At first a shift toward higher peak melting temperatures in the DSC thermogram is also observed, Figure 17. In order to investigate whether or not this is due to changes in the amount of chain

branching, the methyl content was determined, Table II. Corrections were thereby made for CH_3 groups at the ends of the main chains. The untreated polymer is assumed to contain methyl endgroups only, since the vinyl content is low, Figure 15. Chain scissions during degradation will produce an equal amount of methyl and unsaturated chain ends, however, reactions (28) and (10) in Figure 18. The following correction was thus applied:

$$U_{corr} = U - 14,000[1/\bar{M}_{n_0} + 1/\bar{M}_n]$$

where $\bar{M}_{n_0} = \bar{M}_n$ for the untreated sample and $U = CH_3/1000\ C$.

As shown in Table II, the methyl content changes in a complicated way, showing a considerable drop after long heating time. This cannot be correlated to the fairly small and regular changes in the vinylidene content. Obviously, there is no correlation between the changes in methyl content and the changes in the DSC thermograms either, Figure 17. After 6–12 min of degradation, the peak melting temperature increases from 384°K to 387°K. Heating for 24 min results in the simultaneous redevelopment of the peak at 384°K. Such changes were also observed in pure thermal degradation,[1] and the same explanation is supposed to be valid: chain scission will give an increased amount of shorter, more mobile chains which are more apt to form a more ordered structure. With increasing chain scission, this tendency will be counteracted by the effect of the increased amount of chain ends, internal olefinic unsaturation, and oxygen-containing groups. After 48 min of heating, the high content of anomalous structures prevents the formation of the high melting peak. At the same time, a lower melting peak at 380°K develops. This might be due to the considerable amount of carbonyl groups present, since it is known[18] that carbonyl groups can participate in highly ordered structures of PE.

Interpretation of Viscometric Measurements

As shown in our previous paper,[1] the degree of LCB must be taken into account in the interpretation of the results of the determination of the intrinsic viscosity in the degradation of PE. Otherwise, the interpretation may result in great inaccuracies. At 284°C, $\bar{M}_w$'s increase, Table I. The intrinsic viscosity decreases, however (Fig. 1), as a result of the increase in LCB (Figs. 9 and 10). This increase is larger in the presence of oxygen. At 355°C, the drop in intrinsic viscosity is due both to a decrease in $\bar{M}_w$ and an increase in λ. The relative effect of an increase in λ on the intrinsic viscosity rapidly decreases at higher λ levels.[4] As a result, the differences in the intrinsic viscosity after degradation with or without oxygen at 355°C are hardly influenced by the difference in λ, but are roughly proportional to the difference in $\bar{M}_w$.

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