

**Thermal Degradation of Polyethylene in a  
Nitrogen Atmosphere of Low Oxygen Content.  
II. Structural Changes Occurring in Low-Density  
Polyethylene at an Oxygen Content  
Less Than 0.0005%**

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**Synopsis**

Samples of low-density polyethylene, free from additives, were heated at temperatures between 284° and 355°C under high-purity nitrogen. Changes in molecular weight distribution (MWD), molecular weight averages, 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). At 284° and 315°C, the MWD's were shifted toward higher molecular weights and the  $\bar{M}_w$  values increased. At 333° and 355°C, the MWD's shift toward lower molecular weight, but the high molecular weight tail is largely retained.  $\bar{M}_w$  decreases slowly at 333°C. At 355°C,  $\bar{M}_w$  undergoes a rapid initial drop which levels off.  $\bar{M}_w/\bar{M}_n$  and the degree of LCB increase with heating time and temperature. Olefinic unsaturation increases. The vinyl groups show a larger relative increase than do the *trans*-vinylene and vinylidene groups. At 355°C, the peak of the unimodal DSC thermogram is shifted to ~3°C higher temperature. A lower melting peak then develops, and after 72 and 90 min the two peaks are about equal in size. The density increases from 0.922 g/cm<sup>3</sup> to 0.930 g/cm<sup>3</sup> for samples heated at 355°C, and the weight loss was 1.5% after 90 min. A reaction scheme for the thermal degradation of polyethylene is discussed. Initiation is suggested to be accomplished by scission of allylic C-C bonds. Propagation proceeds by both intra- and intermolecular hydrogen abstraction, followed by  $\beta$ -scission. Termination can occur by both combination and disproportionation. Combination reactions are suggested to account for the observed formation of LCB and high molecular weight material. Due to changes in the degree of LCB during the degradation, viscometry alone will not give a proper measure of the changes in molecular weight.

**INTRODUCTION**

Although there is much interest today in extruding and injection-molding polyethylene at temperatures up to 350°C,<sup>1</sup> few investigations have been published on the structural changes which may occur in polyethylene when it is subjected to such conditions. In 1949, Oakes and Richards<sup>2</sup> published

their work on low-density polyethylene (LDPE) heated under vacuum at temperatures between 295° and 360°C. Analyses were carried out by viscometry, infrared spectroscopy, and some chemical methods. Quackenbos<sup>3</sup> treated high-density polyethylene (HDPE) in nitrogen and nitrogen containing 0.34% oxygen and followed the changes in intrinsic viscosity and carbonyl content. Arnett and Stacy<sup>4</sup> heated HDPE in a vacuum and measured the changes in average molecular weight by ebullioscopy and, for a few samples, by light scattering. In all cases, the observed changes are in accordance with the common view that polyethylene degrades according to a random scission type of mechanism. By using gel chromatography (GPC) when investigating the thermal degradation of LDPE,<sup>5</sup> we were able to follow the changes in molecular size in greater detail. The results obtained were difficult to explain quantitatively with a random scission type of mechanism.

The opinion that polyethylene is degraded according to a random scission mechanism was expressed by Wall<sup>6</sup> in 1948. He came to this conclusion after analyzing volatile products from LDPE heated at 400°C under vacuum. He proposed an initial random homolytic scission of the polymer chain followed by random intermolecular hydrogen abstraction and subsequent  $\beta$ -scission of the chain attacked in this second step.

Subsequently, some important additions to this theory have been made:

1. The existence of weak links. These cause the degradation to start at 100°C lower temperature than expected.<sup>2</sup> Weak links were also assumed to be responsible for the high initial rate of weight loss and drop in intrinsic viscosity.<sup>2,7</sup>

2. An intramolecular hydrogen abstraction (back-biting) running parallel to the intermolecular one. This could explain both the immediate formation of volatile material and its composition.<sup>7-11</sup>

In a random scission type of degradation, the largest molecules degrade with the greatest probability. As a result, the molecular weight distribution (MWD) will rapidly approach "the most probable distribution" with a value of  $\bar{M}_w/\bar{M}_n$  of 2. Randomly distributed weak links or back-biting will not influence this behavior.

In the above-mentioned investigations, degradation was followed mainly by measuring the rate and composition of volatile material. Changes in chemical structure on residual material were determined by infrared measurements, and changes in molecular size, by viscometry or ebullioscopy. Direct measurements of changes in MWD are obviously of great interest when investigating the degradation mechanisms. We have used GPC measurements to study such changes.

In our previous paper,<sup>5</sup> we reported studies on LDPE free from additives heated between 284° and 355°C. The GPC measurements were supplemented with intrinsic viscosity determinations. This gave us an opportunity to compare our measurements with previously published results. We found that the  $\bar{M}_w/\bar{M}_n$  did not decrease and that the high molecular weight material did not disappear even when average molecular weights and in-

trinsic viscosity had been substantially reduced. This indicates that molecular enlargement reactions play an important role in polyethylene degradation. A major question in connection with this is whether the degree of long-chain branching (LCB) changes or not. In the present study, this has been investigated, together with MWD measurements. A method devised by Drott<sup>12</sup> has been used where GPC and viscosity measurements are combined. The structural changes during degradation have been further investigated by the use of infrared spectroscopy (IR) and differential scanning calorimetry (DSC).

## 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 additives. It has the following characteristics: density, 0.922 g/cm<sup>3</sup>; melt index, 0.31 g/10 min;  $[\eta]_{p-xy1}^{105^{\circ}\text{C}} = 1.06$  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 used in this study was delivered by AGA AB, Göteborg, Sweden, and is reported to contain 0.00028% by volume 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 to control the temperature to better than  $\pm 1^{\circ}\text{C}$  during the experiments. The heating temperatures were 284°, 315°, 333°, and 355°C; the heating times were 6, 12, 24, 48, 72, and 90 min 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.<sup>5</sup>

### 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<sup>3</sup> to 10<sup>7</sup> Å giving good separation in the molecular weight range of interest. For details, see reference 5.

In this work, only the calibration curve for linear polyethylene was needed. It was obtained via the universal calibration curve as described earlier.<sup>5</sup>

The IUPAC characterization round on polymers<sup>13</sup> gave very diverging results and has thus shown the need for reference material. Using the IUPAC HDPE's BMWD and NMWD we obtained:

$$\text{BMWD: } \bar{M}_w = 141 \times 10^3, \bar{M}_n = 12.2 \times 10^3$$

$$\text{NMWD: } \bar{M}_w = 60 \times 10^3, \bar{M}_n = 19.2 \times 10^3$$

The computer program devised by Drott<sup>12</sup> was used to calculate the MWD, molecular weight averages, and the degree of LCB from GPC and viscosity measurements.

In this method, Drott used 0.5 as the exponent for  $g = [\eta]_{\text{br}}/[\eta]_{\text{lin}}$  in the Zimm-Stockmayer equation for trifunctionally branched polydisperse samples.<sup>14</sup> The degree of LCB is assumed to be constant throughout the molecular weight range and is given as  $\lambda = n_w/M$ , where  $n_w$  is the weight-average number of trifunctional branch points per molecule. In this study, we have also used the exponent 0.5.

The choice of 0.5 can be questioned. Drott used narrow fractions of LDPE characterized by light scattering. With the exponent 0.5, he found good agreement between the calculated and experimental calibration curve for GPC. An exponent value of 1.5 gave large deviations. Based on measurements on narrow LDPE fractions with light scattering and viscometry, exponent values of  $1.0 \pm 0.3$  and 1.3 have recently been suggested.<sup>15,16</sup> These values, however, were not used to construct calibration curves that could be compared with the experimental calibration curves of GPC.

It is reasonable to believe that no single value for the exponent exists. The relation might be much more complicated, varying, e.g., with molecular weight and the structure of the branches. However, Drott's method provides the most versatile method thus far for a comparison between long-chain branched samples.

### Viscosity Measurements

Measurements on intrinsic viscosity for LDPE were carried out in 1,2,4-trichlorobenzene at  $135^\circ \pm 0.01^\circ\text{C}$  and in *p*-xylene at  $105^\circ \pm 0.01^\circ\text{C}$ . Like Drott,<sup>17</sup> 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  $135^\circ \pm 0.01^\circ\text{C}$ .

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

### Density and Weight Measurements

Densities at  $23^\circ\text{C}$  were kindly measured by Unifos Kemi AB, Stenungsund, Sweden. The samples ( $\sim 0.2$  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  $8^{\circ}\text{C}/\text{min}$ , the sample size was  $\sim 10\text{--}12$  mg, and the runs were performed in a nitrogen atmosphere. Before being analyzed, all samples were given the same thermal treatment by being heated to  $140^{\circ}\text{C}$  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<sup>13</sup> was utilized as a wedge material. The calibration was then carried out on IUPAC LDPE B with a methyl content of  $28.3 \text{ CH}_3/1000 \text{ C}$ .<sup>13</sup> The other spectra were recorded directly on the films used in the degradation experiments.

### RESULTS

None of the treated samples was discolored nor did any contain insoluble material. Changes in intrinsic viscosity with time and temperature are shown in Figure 1. The relative appearance of the curves is in agreement with earlier findings.<sup>2,5</sup> An initial rapid decrease is followed by a slower change.

In Figures 2 and 3, changes in the MWD are illustrated. Heating for 12 min at  $315^{\circ}\text{C}$  causes an increase in molecular size resulting in a shift of the MWD toward higher molecular weights. An increase of the heating time to 90 min results in a further increase in high molecular weight material, but

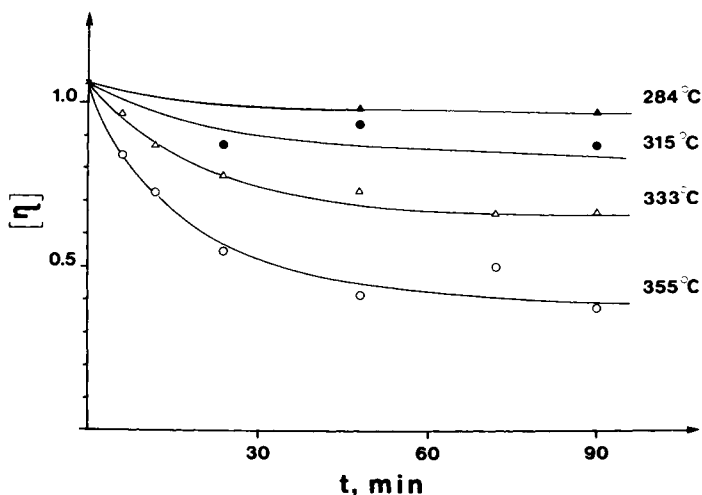


Fig. 1. Change in intrinsic viscosity as a function of heating time and temperature.

at the same time, a reduction in molecular size results in a return to the original MWD for the low molecular weight end. Heating at 284°C for 90 min gives the same general result. At higher temperatures, a shift toward lower molecular weights is observed. An interesting difference in the high molecular weight tail exists between the curves representing 6 and 24 min at 355°C.

The above-mentioned changes in MWD cause  $\bar{M}_w$  to change according to Figure 4. At 355°C,  $\bar{M}_w$  undergoes an initial rapid decrease followed by minor changes. After 90 min,  $\bar{M}_w$  has decreased to about half its original value. At 333°C,  $\bar{M}_w$  slowly decreases. At 315° and 284°C, an increase is observed.

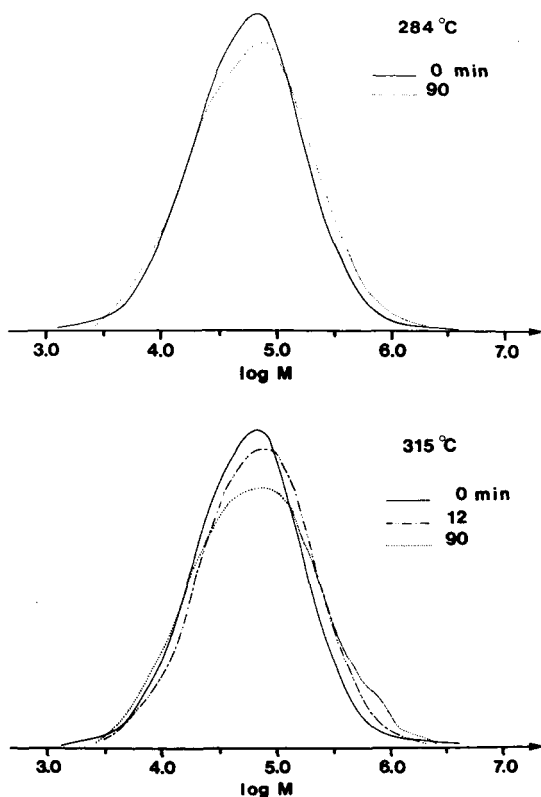


Fig. 2. Change in MWD for samples heated at 284° and 315°C.

Figure 5 shows that  $\lambda$  initially increases with heating time. The increase is larger the higher the temperature. Contrary to this general tendency, no increase is observed during the first 12 min of heating at 355°C.

The changes in  $\bar{M}_w/\bar{M}_n$  are shown in Figure 6. A constant value or an increase is obtained.

In Figure 7, the result of an IR analysis of olefinic unsaturation is shown for untreated polymer and polymer heated for 24 and 72 min at 355°C.

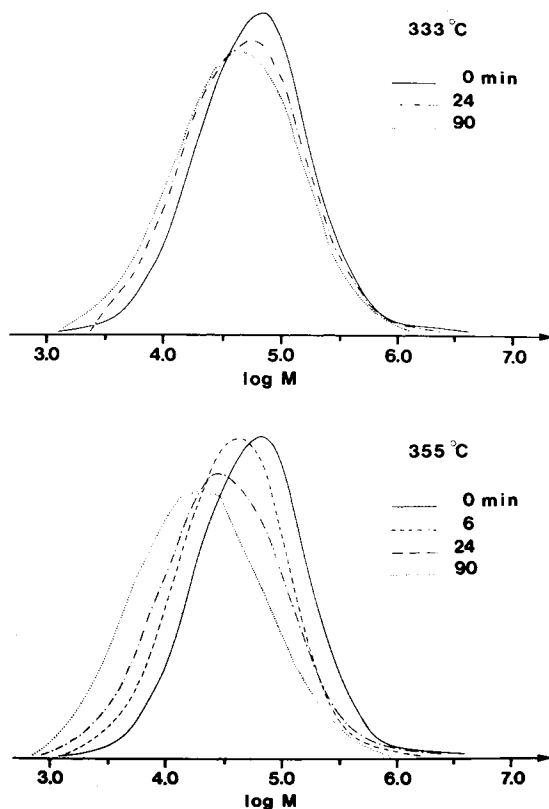


Fig. 3. Change in MWD for samples heated at 333° and 355°C.

The films had the same thickness, 0.25 mm. At lower temperatures, the changes were in the same direction, but smaller in magnitude.

The vinyl groups show a larger relative increase than do the *trans*-vinylene and vinylidene groups. Infrared analyses of carbonyl content were also undertaken using the peak at  $1720\text{ cm}^{-1}$ . The carbonyl content was small in the untreated sample and was slightly reduced during heating.

Determinations of weight losses, methyl contents, and densities of samples degraded at 355°C are summarized in Table I. The weight loss is very small and is in accordance with other reported data.<sup>18,19</sup> A significant drop is noted in the methyl content between 24 and 90 min of heating. The density shows an interesting and significant increase.

The DSC thermograms for samples heated at 355°C are given in Figure 8. The initial unimodal curve is split into a bimodal one. One peak is developed at a  $\sim 3^\circ\text{C}$  higher temperature than the original peak. After 12 min, the lower melting peak is reduced to a small shoulder. After 72 and 90 min of heating, the peaks are about equal in size. Like the density, the area under the curve shows a tendency to increase with heating time, indicating an increase in crystallinity. At lower temperature levels, no significant changes in the DSC thermograms occur.

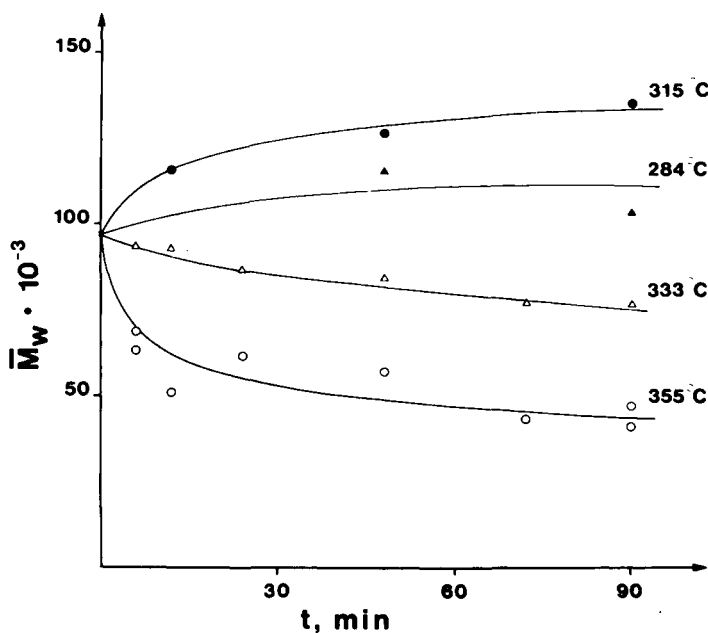


Fig. 4. Change in  $\bar{M}_w$  as a function of time and temperature.

## DISCUSSION

### Initiation

LDPE starts to degrade at about 280°C in an inert atmosphere while, e.g., hexadecane is stable up to 390°C under the same conditions.<sup>2</sup> The presence of olefinic, hydroperoxide, and carbonyl groups, as well as branch points, have generally been put forward as an explanation for this behavior.

The presence of hydroperoxides in LDPE of the actual type has never been reported. Thus, hydroperoxides are not further discussed here as a source of initiation.

Considering the three other types of extraneous structures, it is obvious the C-C bond in the allylic position has the lowest bond dissociation energy, 61.5 kcal/mole (see Table II).

The second weakest point is the position alpha to the carbonyl. The difference in bond dissociation energy between these two structures is ~10 kcal/mole. On the assumption that the bond dissociation energy is equal to the activation energy ( $E_a$ ) and the factor  $A$  in the Arrhenius equation,  $k = A \cdot e^{-E_a/RT}$ , is the same, a 3000-fold difference in bond dissociation rate at 350°C is found.

Since our results clearly show that the olefinic groups increase during degradation (Fig. 7), there is no reason to believe that weak points other than labile allylic C-C bonds should act as initiation points at temperatures below 360°C in an inert atmosphere.



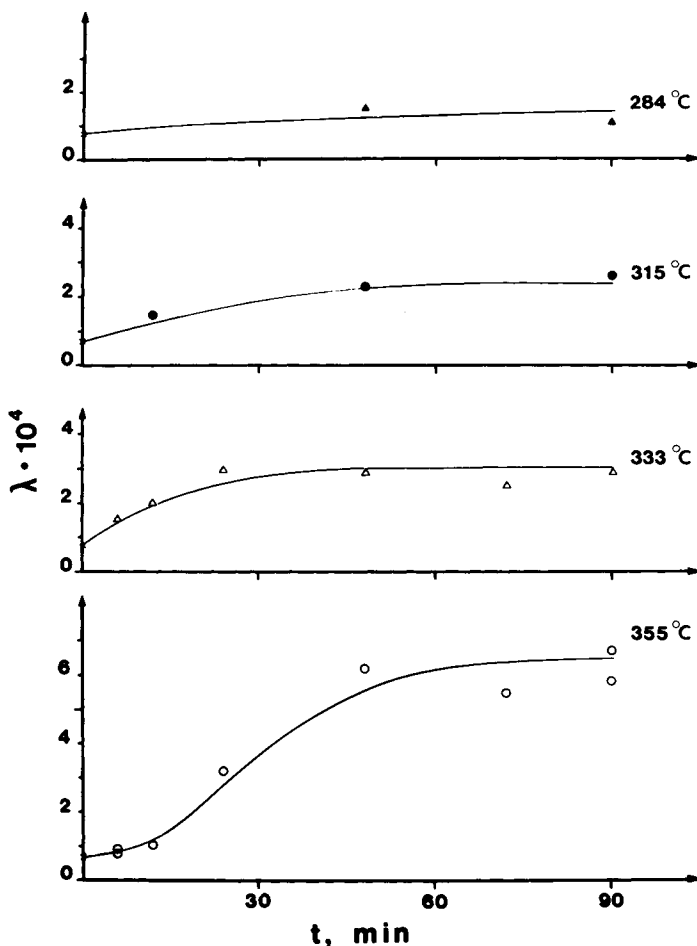
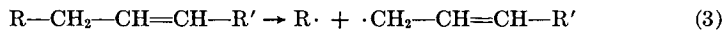
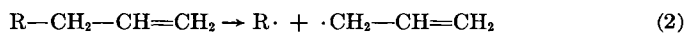
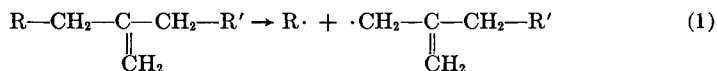


Fig. 5. Change in degree of LCB ( $\lambda$ ) as a function of time and temperature.

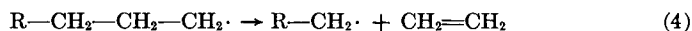
As a result, the following initiation reactions should be most important:



### Propagation

A primary radical formed will undergo either of the following three propagation reactions: depolymerization or intra- or intermolecular hydrogen abstraction.

Depolymerization via  $\beta$ -scission:



where  $E_a$  of model compound  $\approx 26$  kcal/mole.<sup>22</sup>

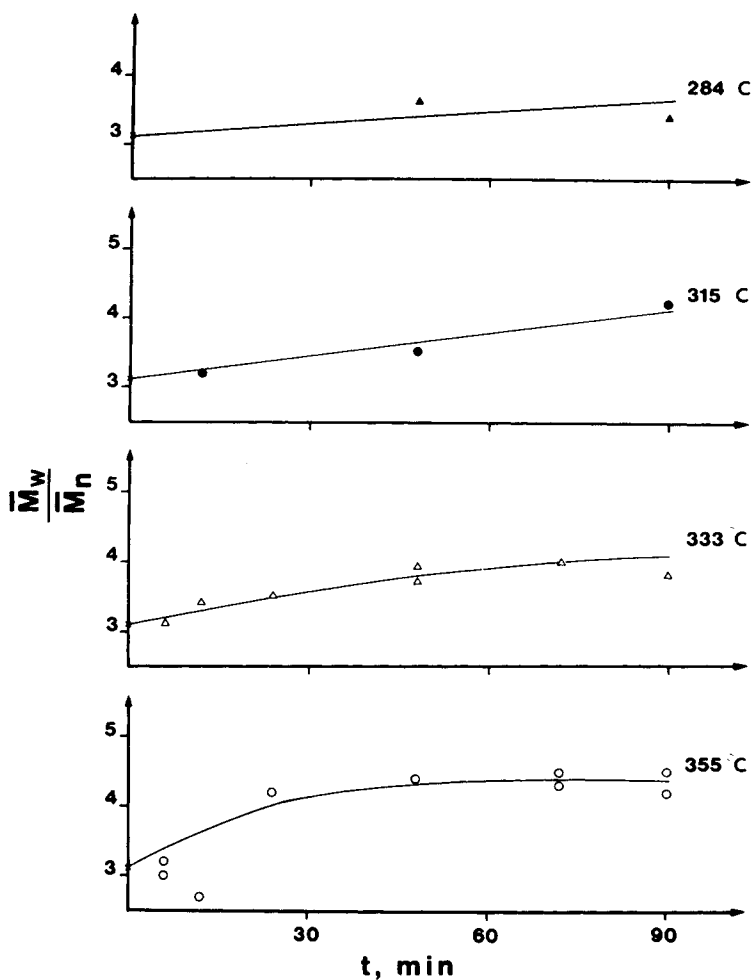
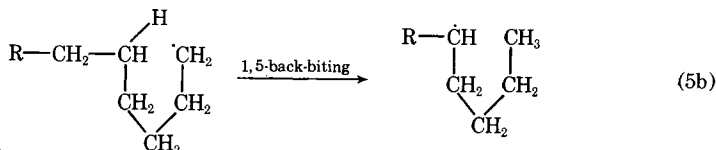
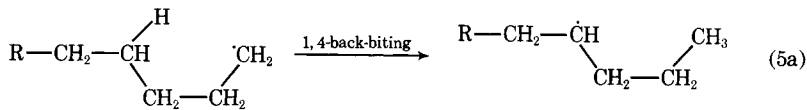


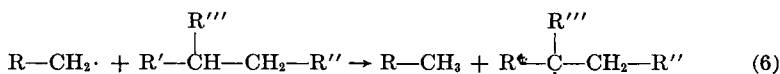
Fig. 6. Change in  $\bar{M}_w/\bar{M}_n$  as a function of time and temperature.

Intramolecular hydrogen abstraction (back-biting)<sup>7,9,10,11,23</sup>:



where  $E_a$  for hydrogen abstraction by a primary radical  $\approx 10$  kcal/mole.<sup>22</sup>

Intermolecular hydrogen abstraction:



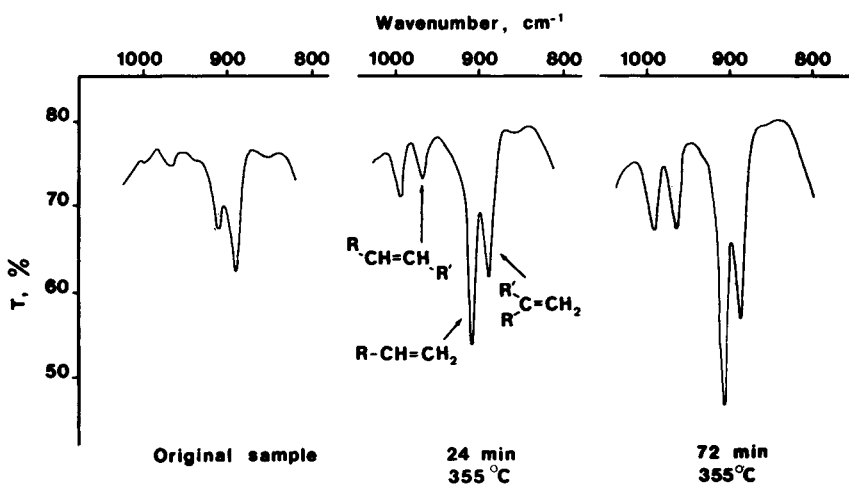


Fig. 7. Changes in the infrared spectra for samples heated at 355°C.

TABLE I  
Weight Loss, Methyl Content, and Densities for LDPE Samples Heated at 355°C

Heating time, min	Weight loss, % of original sample	Methyl content, CH <sub>3</sub> /1000 C		Density, g/cm <sup>3</sup>
		Uncorrected	Corrected <sup>a</sup>	
0	0	21	20	0.922
6	0.7	24	22.5	0.924
12	0.8			
24	0.9	24	22.5	0.930
48	1.2			
72	1.4			
90	1.5	17	15	0.929

<sup>a</sup> The untreated polymer is assumed to contain methyl endgroups only. Chain scissions during degradation will produce an equal amount of methyl and unsaturated chain ends, however. The following correction was thus applied:

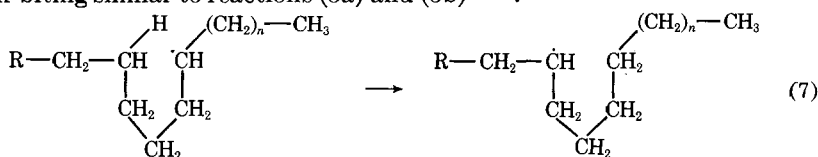
$$\text{corrected value} = \text{uncorrected value} - 14,000 \times (1/\bar{M}_{n_0} + 1/\bar{M}_n)$$

where  $\bar{M}_{n_0}$  is equal to  $\bar{M}_n$  for the untreated sample.

where R, R', and R'' = alkyl groups; R''' = hydrogen or alkyl group.  $E_a$  for hydrogen abstraction by a primary radical  $\approx 10$  kcal/mole.<sup>22</sup>

The radicals formed by back-biting according to reaction (5) may undergo further propagation steps as follows:

Back-biting similar to reactions (5a) and (5b)<sup>11,23</sup>:



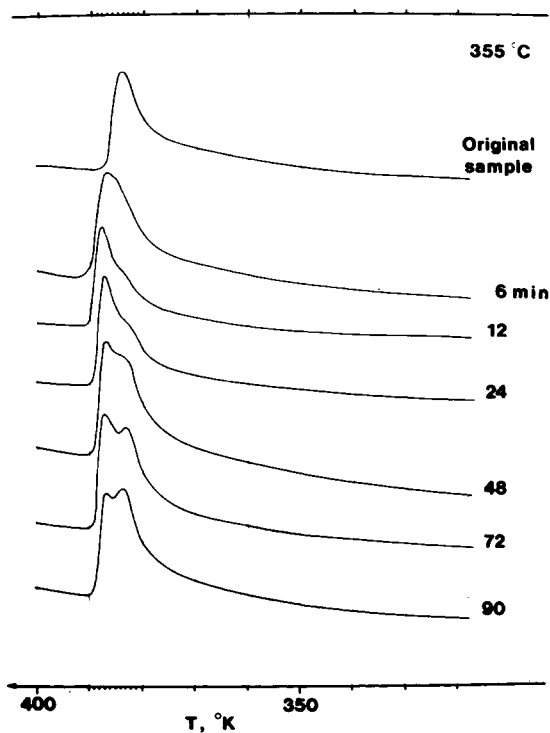
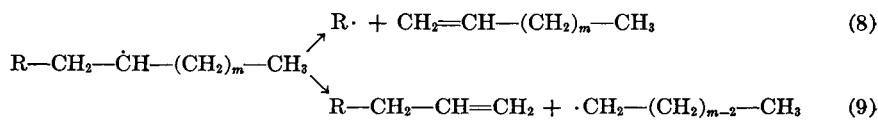


Fig. 8. DSC thermograms for samples heated at 355°C.

TABLE II  
Bond Dissociation Energies for C-C Bonds

Structure	Bond dissociation energy for model compound at 25°C, kcal/mole	Ref.
$D(\text{R}-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{R})$	61.5	20
$D(\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{R})$	72	21
$D(\text{R}-\text{CH}_2-\underset{\text{R}}{\text{CH}}-\text{CH}_2-\text{R})$	80	22
$D(\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R})$	87	22

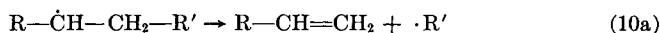
$\beta$ -Scission to the radical site:



where,  $E_a$  for model compound  $\approx 27$  kcal/mole.<sup>22</sup>

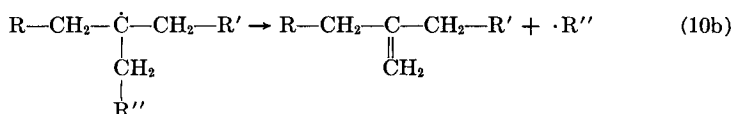
The radicals formed by intermolecular hydrogen abstraction according to reaction (6) may also undergo  $\beta$ -scission. Reactions (10a), (10b), and (10c) were suggested by Oakes and Richards<sup>2</sup> to account for the fact that vinyl, vinylidene, and vinylene groups were found to increase when LDPE was heated.

A secondary radical gives a vinyl group:



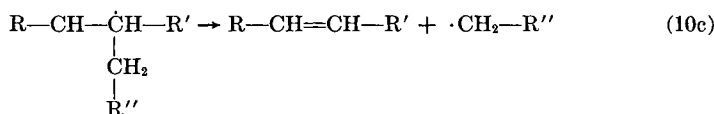
where,  $E_a$  for model compound  $\approx 27$  kcal/mole.<sup>22</sup>

A tertiary radical gives a vinylidene group:

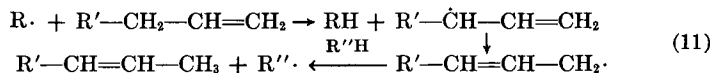


where,  $E_a$  for model compound  $\approx 23$  kcal/mole.<sup>22</sup>

A secondary radical alpha to a branch point gives a vinylene group:



Another possibility for the formation of vinylene groups is:



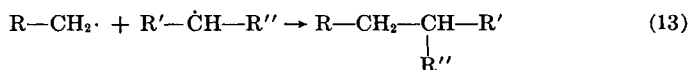
The abstraction of hydrogen from the allylic position should be highly favored compared to abstraction of secondary bonded hydrogen or addition of the free radical to the double bond at temperatures above 300°C.

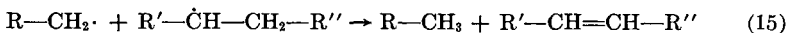
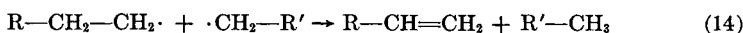
Analysis of volatile material by gas chromatography has convincingly shown that intramolecular hydrogen abstractions followed by  $\beta$ -scission, reactions (5), (7), (8), and (9), are important propagation reactions around 400°C.<sup>9-11</sup> These reactions, however, exert only a minor influence on changes in average molecular weight.

Propagations by intermolecular hydrogen abstraction followed by  $\beta$ -scission, reactions (6) and (10), were the propagation reactions considered most important in the degradation of polyethylene. These reactions would cause a large decrease in average molecular weight before any volatiles are produced.

### Termination

The following combination and disproportionation reactions are considered to be the most important under our conditions:





$E_a$  for reactions (12)–(15) is almost 0 kcal/mole.<sup>24</sup> Both combination and disproportionation are known to occur.<sup>25–29</sup> It is also well known that the tendency to disproportionation will increase with temperature.<sup>26,30</sup>

For primary radicals, reactions (12) and (14), it has been estimated that combination is about ten times as probable as disproportionation at temperatures between 300° and 400°C.<sup>4</sup> In the case of a reaction between primary and secondary radicals, the disproportionation reactions will be more important.<sup>30</sup>

Since radical addition to olefinic groups is not considered probable under our conditions, reactions (12) and (13) will be the only way in which larger and more branched molecules form. Reactions (8), (9), (10a), and (14) give vinyl groups. Reactions (10c), (11), and (15) give vinylene groups. Reaction (10b) gives vinylidene groups.

## DISCUSSION OF EXPERIMENTAL RESULTS

The LDPE used in this study has a relatively narrow MWD and a low degree of LCB and short-chain branching (SCB) as compared to LDPE produced in autoclave reactors. We have not measured the amount of olefinic groups quantitatively. For this type of material, the following values have been quoted as typical: 0.3–0.7/1000 C for vinylidene, ~0.1/1000 C for vinyl, and ~0.1/1000 C for *trans*-vinylene.<sup>31,32</sup>

### Intrinsic Viscosity

The generally accepted view that heat treatment of polyethylene in the studied temperature range results in a rapid decrease in molecular weight according to a random scission type of degradation (see, e.g., Hawkins<sup>33</sup>) is based on viscometric measurements only. Conclusions based solely on such measurements result in undue simplifications. Intrinsic viscosity is not directly related to the number and molecular weight of molecules. Furthermore, at constant  $\bar{M}_w$  it is tremendously sensitive to the degree of LCB.<sup>14,34</sup>

Our viscometric measurements, Figure 1, show a decrease at all temperatures in accordance with previous findings.<sup>2,5</sup> The degree of LCB, calculated from GPC and viscometric data, increases at all temperatures (Fig. 5). GPC data, corrected for the degree of LCB, result in the MWD's shown in Figures 2 and 3. Corresponding  $\bar{M}_w$  values are given in Figure 4. Obviously, no general decrease in molecular weight occurs. On the contrary, the results illustrate the competitive processes of chain scission and molecular enlargement which are indicated in the proposed reaction scheme, reactions (1)–(15).

The apparent discrepancy between the increase in  $\bar{M}_w$  and the decrease in intrinsic viscosity at 284° and 315°C illustrates the great depressing influence that an increase in the degree of LCB has on the intrinsic viscosity.

At 333° and 355°C, a decrease in  $\bar{M}_w$  and an increase in the degree of LCB cooperate to reduce the intrinsic viscosity.

In our previous paper,<sup>5</sup> the intrinsic viscosity and  $\bar{M}_w$  data, uncorrected for LCB, were utilized for the calculation of  $E_a$  for the thermal degradation of LDPE. The results obtained were in good agreement with several published  $E_a$  values from thermogravimetric measurements.<sup>19,35,36</sup>

In view of the results presented above, neither the intrinsic viscosity nor the uncorrected  $\bar{M}_w$ 's would be a proper measure of the (overall) reaction rate. The same objections can be raised against measurements of weight loss. Further, formation of volatiles and molecular weight changes as reflected by the intrinsic viscosity are not caused by the same reactions.

The reason for the agreement between our  $E_a$  data and those obtained from thermogravimetric measurements is thus not obvious. In both cases, however, the temperature dependence of the observed quantities is the same.

### Molecular Weight Distribution and Long-Chain Branching

The MWD's and the  $\bar{M}_w$ 's for the samples treated at 284° and 315°C (Figs. 2 and 4) demonstrate a net increase in high molecular weight material. The effect is largest at 315°. At these temperatures the molecular enlargement reactions, reactions (12)–(13), apparently dominate over chain scission, reaction (10). At 333° and 355°C (Figs. 3 and 4), the MWD's and  $\bar{M}_w$ 's shift toward lower molecular weights. Thus, chain scission will begin to dominate in the temperature range of 315° to 333°C.

Although the MWD's shift rapidly downward at 355°C, the high molecular weight tail is largely retained. The large increase in LCB ( $\lambda$ ), shown in Figure 5, indicates that this is due to molecular enlargement reactions occurring parallel to chain scission even at this temperature. At lower temperatures, the enlargement reactions are also evidenced by increases in  $\lambda$ . Combinations involving a secondary radical leading to branching are much less probable than combinations of primary radicals. Thus, any increase in  $\lambda$  is evidence of a substantial amount of molecular enlargement reactions.

A significant deviation from the general pattern is the low and constant value of  $\lambda$  after 6 and 12 min of degradation at 355°C. This indicates that at this temperature, chain scission is more dominant at the beginning of the degradation than it is later on. The increase in  $\lambda$  between 6 and 24 min at 355°C is in agreement with the somewhat larger high molecular weight tail in the MWD observed after 24 min in Figure 3.

The formation of high molecular weight material parallel to chain scission broadens the MWD's and causes  $\bar{M}_w/\bar{M}_n$  to increase (Fig. 6). This behavior is contrary to that expected for a random scission type of degradation.

### Weight Loss

The small weight losses observed, Table I, are in good agreement with earlier published data.<sup>18,19</sup> (Note: The weight loss data reported in our

previous paper<sup>5</sup> corresponded to 0.28% oxygen and not to 0.0063% oxygen as stated.) The volatiles can, in principle, be formed by all the reactions suggested which include scission of C-C bonds. Depolymerization, reaction (4), with scission  $\beta$  to a primary radical is *per se* quite possible since  $E_a$  is about 26 kcal/mole. Transformation of the primary radical to a secondary one by intra- or intermolecular hydrogen abstraction, reactions (5) and (6), is, however, more highly favored since  $E_a$  is only  $\sim 10$  kcal/mole. Bailey et al.<sup>9,10</sup> and Tsuchiya and Sumi<sup>11</sup> have convincingly shown that, around 400°C, the intramolecular hydrogen abstractions followed by  $\beta$ -scission, reactions (5), (7), (8), and (9), account for the main part of the volatile material, while depolymerization accounts for about 10%. Intermolecular abstraction was not important for the formation of volatiles. It seems reasonable to assume that their results are valid under our conditions also.

When polyethylene is put forward as a typical example of a polymer undergoing random scission,<sup>33,37</sup> results obtained by Wall and co-workers are often quoted (see, e.g., Wall et al.<sup>38</sup>). Upon heating polymethylene with  $[\eta]_{p-xy}^{120^\circ\text{C}} = 20$  dl/g between 375° and 400°C, they found that the intrinsic viscosity had dropped to 2% of its initial value when 1% volatile material had been formed.

We observed, under our conditions, no such effects with LDPE (Table I). After 90 min at 355°C, about 1.5% of volatile material is formed, but the intrinsic viscosity has only been reduced to about 40% of its initial value. The reason for the difference could be ascribed to the influence of LCB on the intrinsic viscosity. For a linear polymer like polymethylene, even a small increase in  $\lambda$  will have tremendous effects.

### Olefinic Unsaturation

The formation of olefinic groups during the degradation of LDPE was reported by Oakes and Richards.<sup>2</sup> Our results (Fig. 7) are in agreement with their findings. All three types of unsaturation increase. In the original sample, vinylidene dominates over vinyl, but after 24 and 72 min the situation is reversed. The *trans*-vinylene peak increases from being barely detectable in the original sample to about the same size after 72 min as the initial vinyl peak. Oakes and Richards suggested reactions (10a) to (10c) to account for the observed results. In addition to reaction (10a), vinyl groups can also be formed by scission after intramolecular transfer according to reaction (9) and by disproportionation between primary radicals, reaction (14). Reaction (8) also results in vinyl groups. However, they are located in small volatile molecules.

Vinylene unsaturation can be formed by other reactions than that proposed by Oakes and Richards, reaction (10c). Isomerization of a vinyl group, reaction (11), and disproportionation between a primary and a secondary radical, reaction (15), will also give vinylene unsaturation. In our view, formation of vinylene by reactions (11) and (15) should be more



probable than a reaction requiring the creation of a radical site alpha to a tertiary carbon atom.

At 355°C, the methyl content first increases and then decreases (Table I). The increase is much larger than that expected from the decrease in  $\bar{M}_n$  or the increase in  $\lambda$ . A possible explanation is the formation of SCB by combination, reaction (13).

### DSC Thermograms

Although the methyl content increases, an increase in density (Table I) and in the area under the DSC thermogram (heat of fusion) (Fig. 8) is observed. The seemingly conflicting situation that density and crystallinity increases at the same time as branching could be explained by the fact that a considerable amount of low molecular weight material is simultaneously formed (Fig. 3). These shorter, more mobile molecular chains will have an increased probability of attaining more ordered structures. The shift in peak temperature of the thermogram could be a further result of these changes.

As mentioned above, the methyl content undergoes a considerable drop between 24 and 90 min of heating. The density and the heat of fusion remain at about the same level. A second lower melting peak develops in the thermogram, however. Even in this case, seemingly conflicting results are obtained. However, no increase in crystallinity should be expected when SCB's are eliminated. As seen from reaction (10b), vinylidene groups remain which might well disturb the close-packing ability in the same way as SCB's. Furthermore, the amount of olefinic groups and chain ends will increase. These changes might offer an explanation in part for the observed phenomena. Further investigations in this area are in progress.

### CONCLUSIONS

When LDPE free from additives is heated under nitrogen in the temperature range 284–355°C, the observed molecular changes are not consistent with a random scission type of degradation. Instead, both chain scission and molecular enlargement reactions occur. The latter will partly result in long-chain branches, which will strongly influence the relationship between  $[\eta]$  and  $\bar{M}_w$ . This has previously not been taken into account when interpreting the rapid drop of the intrinsic viscosity in polyethylene degradation.

The molecular enlargement reactions are found to dominate at 284° and 315°C, and chain scission, at 333° and 355°C.

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