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THERMAL DEGRADATION OF POLYETHYLENE IN A NITROGEN ATMOSPHERE OF LOW OXYGEN CONTENT

I. CHANGES IN MOLECULAR WEIGHT DISTRIBUTION

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SUMMARY

Unstabilised samples of low-density polyethylene were heated in nitrogen containing small amounts of oxygen. The changes in molecular weight distribution were followed by gel permeation chromatography and intrinsic viscosity. A threshold temperature was found at 315° and a threshold oxygen concentration in the range 410–1000 p.p.m.

In accordance with the theory of random scission, degradation caused a shift of the peak position towards lower molecular weights and an increasing skewness of the molecular weight distributions within the original molecular weight limits. No drastic drop of \bar{M}_w/\bar{M}_n was observed.

A simplified method for the construction of gel permeation chromatography calibrations for low- and high-density polyethylene, from measurements on polystyrene standards, is demonstrated. The method is based on the concept of "universal calibration".

INTRODUCTION

Since 1949, when OAKS AND RICHARDS published their work¹, little has been published on the structural changes of low-density polyethylene (LDPE) when heated between 200 and 400°. Work has been done, however, at temperatures below 200°, mostly in air or other oxygen rich atmospheres. In most of these studies the aim has been to investigate the oxidative changes of polyethylene when heated at temperatures in the neighbourhood of its melting point. These studies are of value when evaluating degradation at ordinary processing conditions. A survey of such studies was recently published by REICH AND STIVALA².

In order to elucidate the decomposition mechanism a few studies^{3–7} have been carried out in high vacuum at 400° or above.

OAKS AND RICHARDS¹ performed their experiments on LDPE in vacuum at temperatures from 295 to 360°. They followed the changes in molecular weight by viscosity measurements, and in addition they analysed the chemical structure by infrared spectroscopy and iodine number. The decomposition of LDPE has also been

followed by ordinary non-isothermal thermogravimetric (TGA) measurements. ANDERSON AND FREEMAN⁸ carried out their experiments in a vacuum and IGARASHI AND KAMBE⁹ operated in nitrogen and air whereby activation energies were calculated.

The temperature range between 200 and 400° is of practical importance because modern extruders work in this high temperature range. Moreover, the polymer melt is kept at this high temperature in the reactor during the high-pressure polymerisation process.

Structural changes in HDPE, when heated between 300 and 400°, have been the subject of two important investigations published in 1966. QUACKENBOS¹⁰ treated the HDPE in nitrogen and nitrogen containing 0.34 % oxygen and followed the changes in intrinsic viscosity and carbonyl content.

ARNETT AND STACY¹¹ heated HDPE in a vacuum and measured the changes in molecular weight by intrinsic viscosity and ebullioscopy. They treated their data kinetically and established that the hypothesis of a constant probability of bond scission per unit time (random scission) fits the observed decrease in molecular weight with heating time, if the decrease in bonds breaking is taken into account.

Our work concerns structural changes occurring in LDPE when heated to temperatures between 280 and 360° in atmospheres containing 0.3 % oxygen and less. The results of gel permeation chromatography (GPC) measurements and intrinsic viscosity determinations are reported in this paper.

EXPERIMENTAL

Samples

Nine narrow-distribution standards of polystyrene (PS), \bar{M}_w : 5 · 10³–2145 · 10³, supplied by Waters Associates and four narrow-distribution hydrogenated polybutadienes, supplied by Phillips Chemical Co. were used. The LDPE resin (sample A) was an ordinary quality high pressure resin, free from additives. It was kindly supplied by Unifos Kemi AB (Stenungsund, Sweden):

Density: 0.9210 (g/cm³)

Melt index: 0.24 (g/10 min)

\bar{M}_w : 164 · 10³ (from GPC)

\bar{M}_w/\bar{M}_n : 6.8 (from GPC)

$[\eta]_{p-xyl}^{105^\circ}$: 0.93 (dl/g).

A 0.3 mm thick film was moulded, from which samples 22 × 45 mm were cut for the degradation experiments. The samples were degassed and stored in a vacuum desiccator.

Solvents

1,2,4-Trichlorobenzene (TCB), purum grade, obtained from Th. Schuchardt, (München, G.F.R.), was distilled and the fraction 213–215° was used. 0.45 g/l Santonox-R was added as antioxidant.

p-Xylene, puriss grade, from Fluka AG (Switzerland) was used without further purification.

Nitrogen–oxygen mixtures

Nitrogen–oxygen mixtures containing 22, 63, 410, 1000, 1900 and 2800 p.p.m. oxygen were supplied by Nordiska Syrgasverken AB (Uddevalla, Sweden). The latter also determined the oxygen concentrations.

Heating device

The tubular oven used was similar to that described by QUACKENBOS¹⁰ (Fig. 1).

This construction met the following requirements: (1) Heating and cooling of sample to the desired temperature within 30 sec; (2) temperature constancy to $\pm 1^\circ$ during the experiment; (3) large sample area; and (4) high gas flow.

The samples were placed on 0.1 mm microscopic cover glasses. Before use, the glasses were washed with chromic acid, distilled water and ethanol, and after that dried and stored in a vacuum-desiccator. The mounted sample was kept in the cold part of the oven for at least 20 min before heating. The gas flow was 90 l/h and heating times ranged from 2 to 90 min.

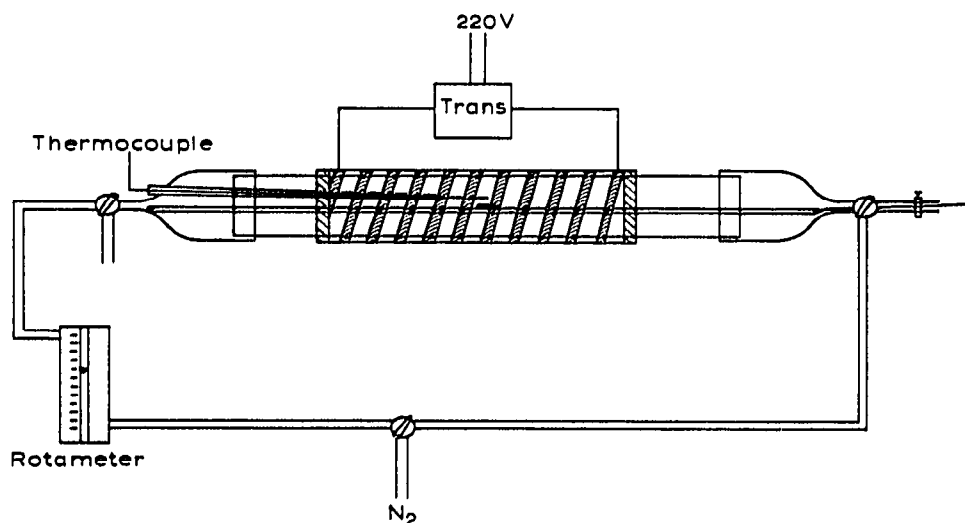


Fig. 1. Heating device.

Thermogravimetric measurements

Thermogravimetric analyses (TGA) were performed with a Mettler thermo-analyser No. 71. Sample size was 6 mg.

Gel permeation chromatography

Waters Associates GPC Model 200 was used. The GPC was equipped with an automatic injection system, a dual-headed pump and an all stainless steel solvent system.

All samples were filtered before injection and all injections were done by the automatic injection system. The experimental conditions were as follows:

Solvent: TCB

Temperature: 135°

Columns: 10^7 , 10^6 , 10^5 , 10^4 , 10^3 Å

Plate count: 1060 plates/ft.

Flow rate: 1.0 ml/min

Sample conc.: 1–4 mg/ml

Injection time: 5 min

Sensitivity: $8 \times$.

Usually GPC determinations of PS-standards and PE-samples were duplicated. As a precaution the only slightly degraded PE-samples were run three times and the undegraded PE-sample A six times. Every second day a control test was done, using a mixture of three completely resolved PS-standards ($\bar{M}_w = 5 \cdot 10^3$, $51 \cdot 10^3$ and $411 \cdot 10^3$).

The baseline-timedrift was small and constant, the noise level *ca.* 1 mm and the reproducibility of \bar{M}_w within $\pm 5\%$.

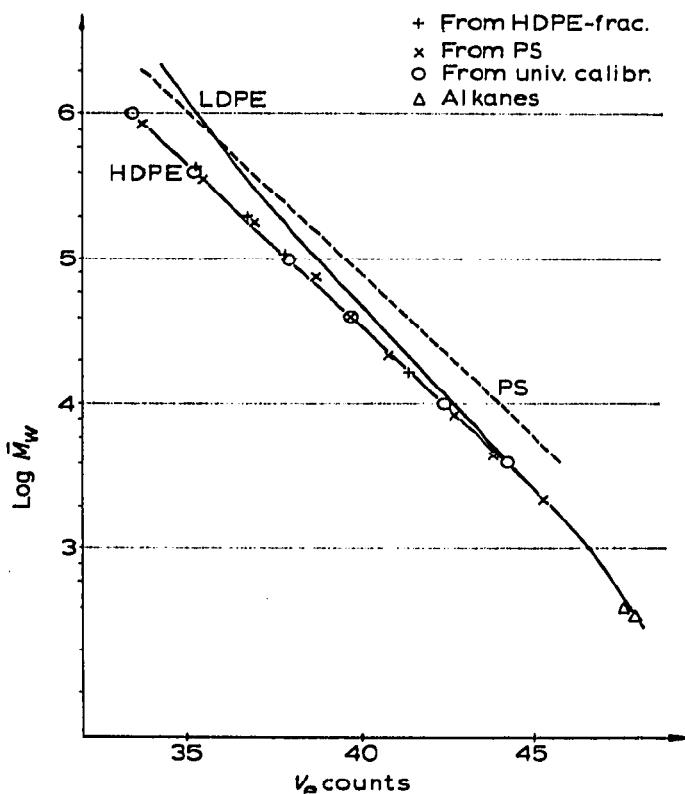


Fig. 2. Calibration curves.

Viscosity

Measurements on intrinsic viscosity for LDPE were carried out in TCB at $135 \pm 0.01^\circ$ and in *p*-xylene at $105 \pm 0.01^\circ$. Like Drott¹³, we found that the solvent systems gave the same result.

Ubbelohde dilution viscometers with flow times of pure solvent greater than 110 sec were used (capillary diam. 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 PS-standards were carried out in TCB at $135 \pm 0.01^\circ$.

Calibration

Calibration curves for PS, LDPE and HDPE are shown in Fig. 2. The calibration curve for PS was determined in the usual way by plotting elution volume at peak maximum (V_e) against $\log \bar{M}_w$. The calibration curves for LDPE and HDPE were

not determined in this manner but were computed directly from the PS calibration curve in combination with published PE-data, by using the methods described below. These calculations are based on the concept of using hydrodynamic volume as the key parameter in constructing a "universal calibration curve". BENOIT and co-workers¹² first proposed this concept, using $\log([\eta] \cdot M)$ as a measure of the hydrodynamic volume. They showed that by plotting $\log([\eta] \cdot M)$ against V_e a single curve is given for a variety of polymers (PMMA, polybutadiene, PVC and branched and linear PS). DROTT¹³ and others¹⁴⁻¹⁸ found that this relation is also valid for LDPE and HDPE.

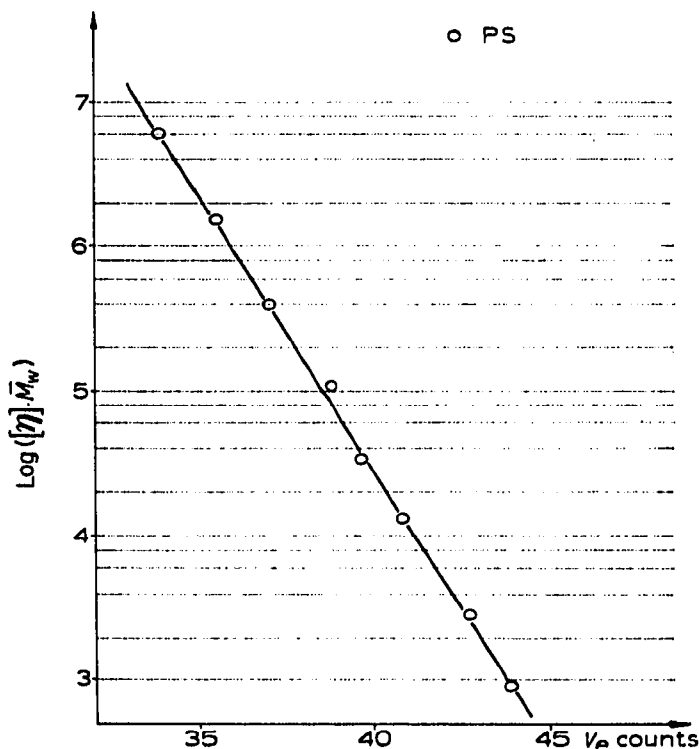


Fig. 3. Universal calibration curve.

By combining data from GPC and viscosity measurements on the PS-standards and using their stated molecular weights, a universal calibration curve has been constructed, (Fig. 3) giving the relation between $[\eta] \cdot \bar{M}$ and V_e .

As this relation should also be valid for PE^{14,18}, the relation between \bar{M}_{PE} and V_e can be calculated if $[\eta]_{PE} \cdot \bar{M}_{PE}$ is known for different values of \bar{M}_{PE} .

For HDPE a Mark-Houwink relationship exists between $[\eta]$ and \bar{M}_w in TCB at 135°. We have used that given by CROUZET¹⁹ *et al.* $[\eta] = 5.23 \cdot 10^{-4} \cdot \bar{M}_w^{0.70}$ to calculate $[\eta]$ and $[\eta] \cdot \bar{M}_w$ for different chosen values of \bar{M}_w . The points thus obtained are shown by \circ in Fig. 2.

Approaching the problem in another way WILLIAMS AND WARD²⁰ found a simple means of constructing a HDPE calibration curve from a known PS-calibration: for every single V_e , $\bar{M}_{PS} = 2.317 \cdot \bar{M}_{HDPE}$. In Fig. 2 such calculations for PS-standards are marked by \times . These points show excellent agreement with the HDPE calibration curve obtained by the method mentioned above. Further confirmation

was obtained by plotting data from the measurements on HDPE-standards (hydrogenated polybutadiene) (Fig. 2. (+)).

So far no mathematical expression for the relationship between \bar{M} and $[\eta]$ has been found for the LDPE. DROTT¹³, PANARIS AND PRECHNER¹⁸ and CROUZET *et al.*¹⁹ have published viscosity and light scattering measurements on LDPE-fractions, using TCB-solutions at 135° for the viscosity measurements. We have utilised these values to construct a $\log \bar{M}_w$ - $\log [\eta]$ relationship (Fig. 4). From this plot it is possible to obtain $[\eta]$ and subsequently calculate $[\eta] \cdot \bar{M}_w$ for different values of \bar{M}_w .

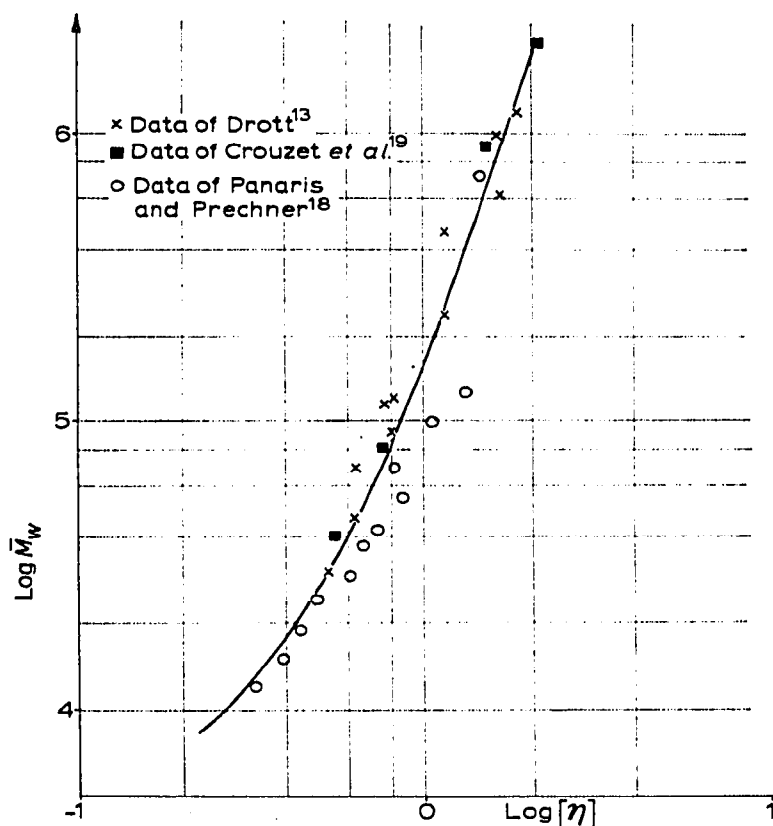


Fig. 4. Relationship between $\log [\eta]$ and $\log \bar{M}_w$ for LDPE.

Using the same calculating procedure as mentioned previously the calibration curve for LDPE (Fig. 2) is obtained *via* the universal calibration curve (Fig. 3). CROUZET *et al.*¹⁹ has published similar calculations starting with data on HDPE and LDPE fractions. The resulting calibration curve for LDPE has the same general appearance and position in relation to the HDPE curve as our LDPE calibration curve.

Treatment of GPC data

Calculation of average molecular weights and plots of weight fraction against $\log M$ (molecular weight distribution (MWD)) from the GPC-curves was carried out by the computer program devised by DROTT AND MENDELSON²¹.

RESULTS AND DISCUSSION

The samples became successively more and more brittle during heat treatment, even at the lowest oxygen levels. The sample treated at the highest temperature, for the longest time in the most oxygen-rich atmosphere acquired a thin brown surface layer. No other sample was discoloured.

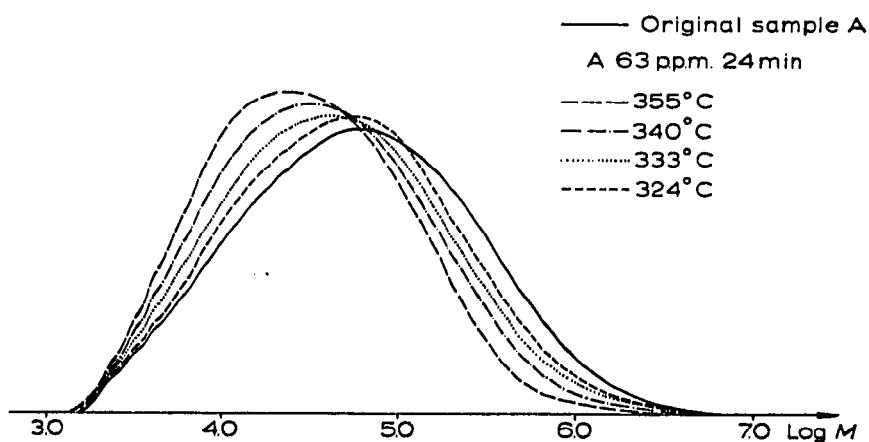


Fig. 5. Weight fraction plotted against $\log M$ (MWD) for sample A, heated for 24 min in 63 p.p.m. oxygen.

None of the samples contained insoluble matter, showing that no (extensive) crosslinking occurred. On the contrary, the heat treatment caused chain scission, clearly demonstrated by a drop in molecular weight (MW), and minor weight losses. The latter effect was followed by TGA-measurements.

In the following paragraphs the effect of temperature, heating time and oxygen content on chain scission is discussed. The experimental work to elucidate time-temperature effects was conducted in 63 p.p.m. oxygen as this low oxygen content gave the same result as oxygen-free nitrogen²².

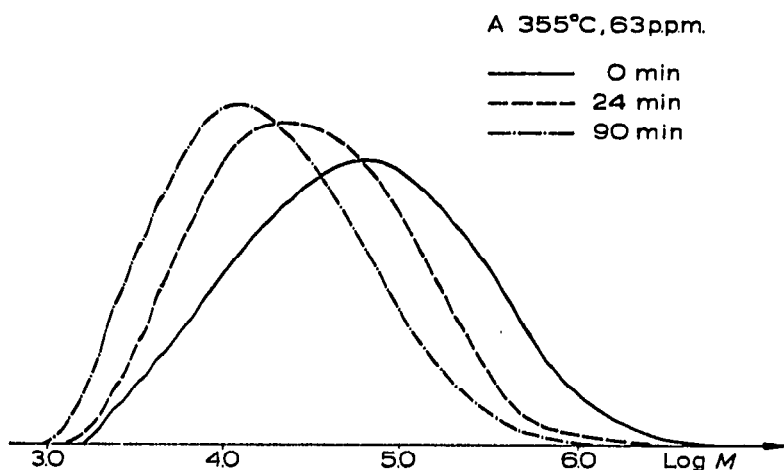


Fig. 6. Weight fraction plotted against $\log M$ (MWD) for sample A, heated at 355° in 63 p.p.m. oxygen.

Effect of temperature and heating time in a nitrogen atmosphere

A series of experiments was conducted in "nitrogen" (63 p.p.m. oxygen). The following time and temperature levels were used (Figs. 5-9 and 13): 2, 6, 12, 24, 90 min; and 284, 315, 324, 333, 340, 355°. Figs. 5 and 6 demonstrate the pronounced effect of temperature and heating time on MWD. The quantity of high molecular weight material diminishes. The highest M -value noticed drops by a factor of two in

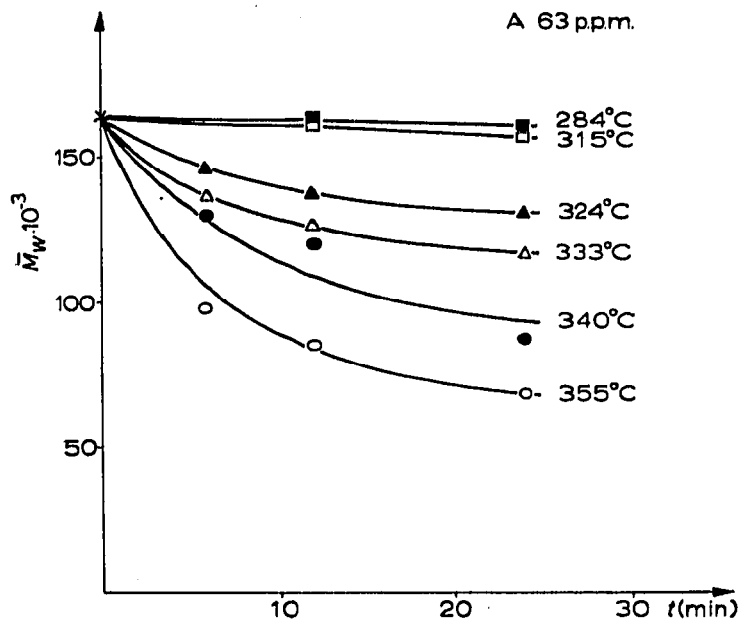


Fig. 7. Change of \bar{M}_w with heating time for sample A heated in 63 p.p.m. oxygen.

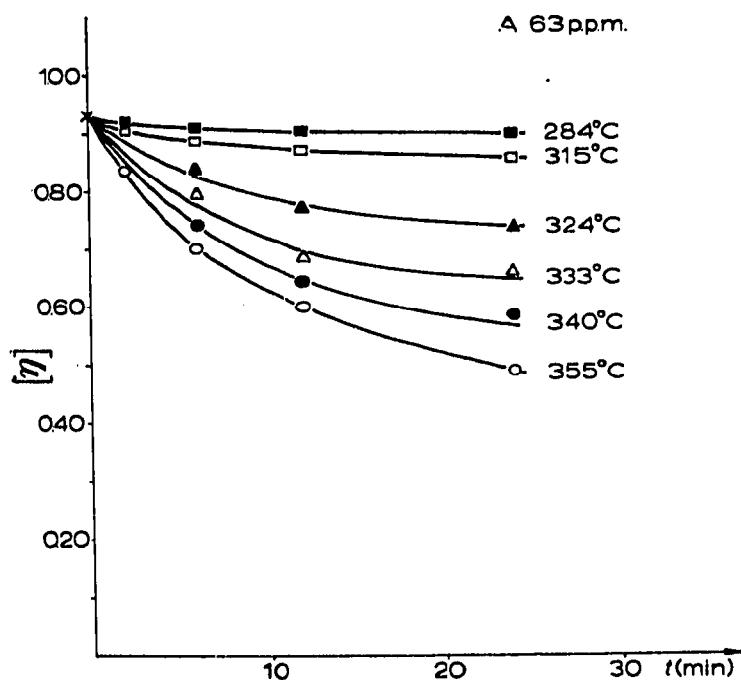


Fig. 8. Change of $[\eta]$ with heating time for sample A heated in 63 p.p.m. oxygen.

each step 0-24-90 min at 355°. However, even after 90 min at 355° material of an M in the order of 10^6 is present.

The low molecular weight end of the MWD is much steeper and does not shift to any appreciable extent up to 24 min at 355°. When the heating time is increased to 90 min, the low molecular weight end drops by a factor of about two. The peak position is moved from $65 \cdot 10^3$ to $12 \cdot 10^3$ and the width of the MWD at 50% peak height is getting smaller.

The TGA-measurements showed the following values:

Time (min)	Temperature (°C)	Weight loss (%)
24	315°	1
24	355°	6
90	355°	17

Fig. 5 shows that a rise in temperature affects the MWD in the same general way as described above for increase in the heating time. The observed changes with time and temperature can be explained qualitatively by the theory of random scission. The high molecular weight end should not vanish completely as the amount of material is small. Thus the MWD is not growing narrower due to the disappearance of the high molecular weight molecules as reported for HDPE¹⁰. According to the random scission

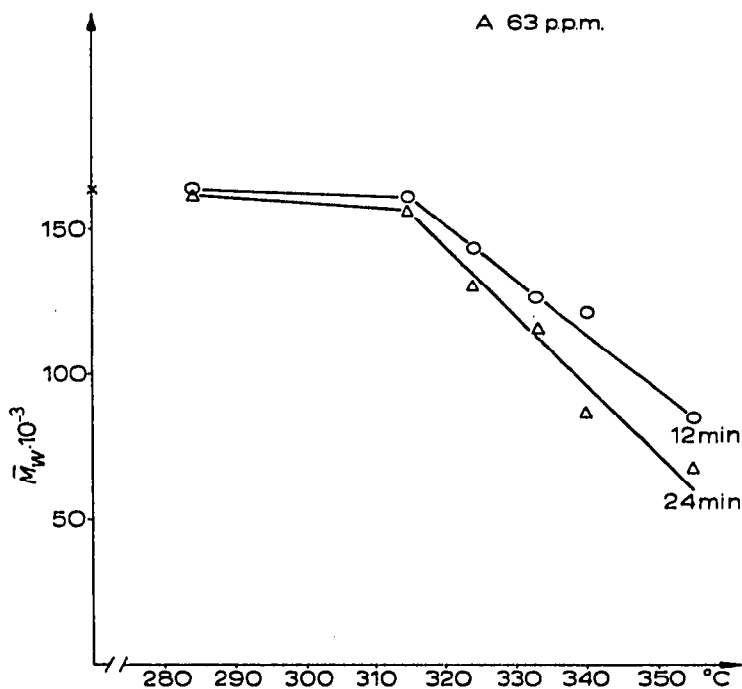


Fig. 9. Change of \bar{M}_w with temperature. Sample A, 63 p.p.m. oxygen.

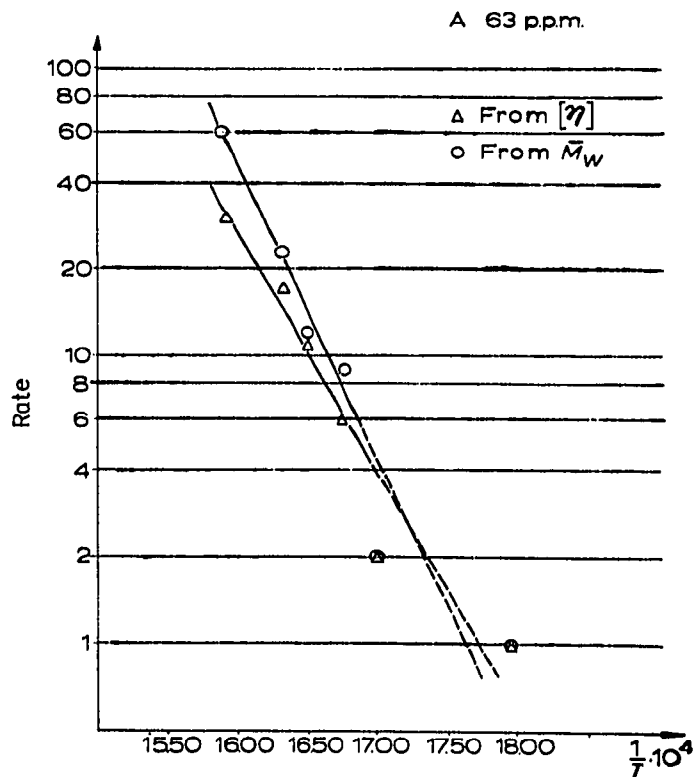


Fig. 10. Arrhenius plot for sample A at 63 p.p.m. oxygen. Data from GPC and viscosity measurements.

theory the main changes will appear in the central part of the MWD, as is observed. The very small changes in the low end and the steepness of the curve is a result of the low statistical probability of bond breaking in a fraction containing small and few molecules.

The fairly large amount of volatile material obtained is not inconsistent with the above reasoning. TSUCHIYA AND SUMI⁷ showed that intramolecular transfer of radicals results in the formation of C₃, C₂, C₄ and C₆ fragments mainly. Thus volatile material is not formed mainly from the low molecular weight tail of the MWD, as proposed by QUACKENBOS¹⁰, but from the whole MWD.

For a more quantitative discussion of the degradation process the \bar{M}_w was calculated. It was supplemented with a determination of $[\eta]$, which also afforded the opportunity of comparison with previously published results. The results are given in Figs. 7 and 8, respectively. Hardly any changes in \bar{M}_w or $[\eta]$ are observed at 284 and 315°. At the higher temperatures the curves are characterised by an initial rapid drop, succeeded by a slower change. Such a degradation course is to be expected for LDPE when being subjected to random scission. This is in accordance with previously published data^{1, 10, 11}. To find the threshold temperature, above which changes are fast, the data were rearranged according to Fig. 9. This plot gave a threshold temperature of 315°, which is in close agreement with data reported for HDPE. (TABAR in ref. 10). The decrease in \bar{M}_w on each side of the threshold temperature follows linear relationships. Like QUACKENBOS¹⁰, who worked with HDPE, we have found that the curves in Figs. 7 and 8 may be super-imposed by sliding the time axis. This time scale can be used as a measure of rate. If the rate is unity at 284° we obtain the following values:

Temperature (°C)	Rate ([\eta])	Rate (\bar{M}_w)
284	1	1
315	2	2
324	6	9
333	11	12
340	17	23
355	30	60

These values have been used in the Arrhenius plot (Fig. 10). Activation energies have been calculated from this plot and we found 64 kcal/mole from $[\eta]$ and 69 kcal per mole from \bar{M}_w . These values are in good accordance with the value of 67 ± 5 kcal/mole given by ANDERSON AND FREEMAN⁸ and also with the values of IGARASHI AND KAMBE⁹ who reported 61 and 74 kcal/mole for a LDPE, from TGA measurements. This means that the activation energy is approximately the same for weight loss and MW-decrease in nitrogen as it is in a vacuum for a LDPE resin. According to our previous discussion on the effect of random scission on changes in MWD, this is a further indication that TSUCHIYA AND SUMI's theory⁷ on intramolecular transfer of radicals is valid. The highest probability, by far, is in the medium molecular weight range. Thus the scission of the molecules in this part of the MWD causes both the bulk of the changes in \bar{M}_w and $[\eta]$ as well as the bulk of the formation of volatile material.

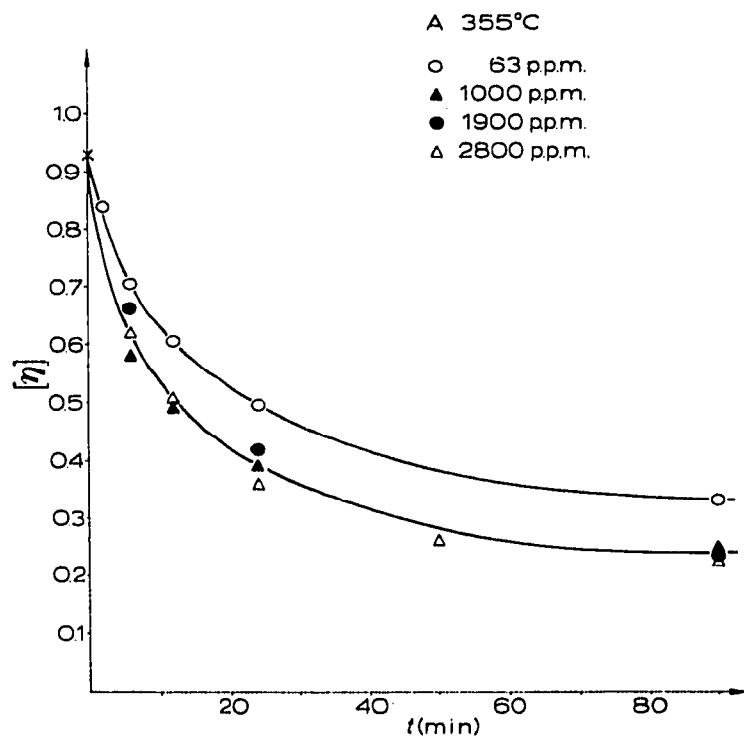


Fig. 11. Change of $[\eta]$ with heating time for sample A heated at 355°

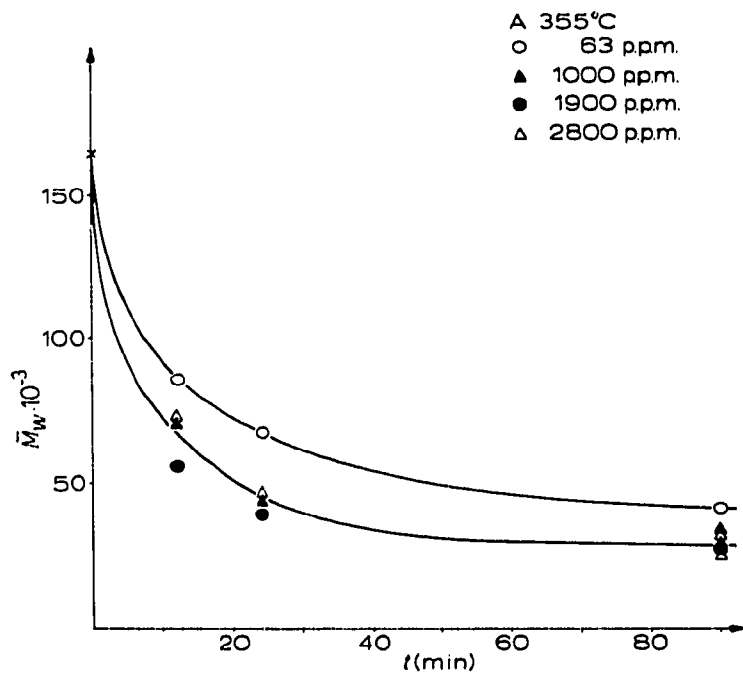


Fig. 12. Change of \bar{M}_w with heating time for sample A heated at 355°.

Effect of oxygen

It is known that the combination of heat and oxygen causes discolouration and formation of odoriferous material while the mechanical and electrical properties of the PE's are declining. In air at temperatures above 250° these changes are very rapid. The present investigation concerns oxygen concentrations below 3000 p.p.m. Changes in MW and MWD will be discussed below, while the changes in chemical structure and crystallinity will be reported elsewhere.

To study the influence of oxygen a series of experiments was conducted at 355°. Heating times were 2, 6, 12, 24 and 90 min and nitrogen containing the following oxygen concentrations was used: 22, 63, 410, 1000, 1900 and 2800 p.p.m. The results are given in Figs. 11-13. Within the range of oxygen concentrations studied an increase in the degradation velocity was observed, but no simple relationship was found. During the investigation we soon found that increasing the oxygen content from 22 to 410 p.p.m. had no effect on the relationship between \bar{M}_w respectively $[\eta]$ and heating time²². Therefore only data from experiments on 63 p.p.m. are given. Furthermore, a similar lack of response was observed on increasing the oxygen content from 1000 to 2800 p.p.m. (Figs. 11 and 12). This means that the experimental results can be summarised in two curves as is shown in Figs. 11 and 12.

The same remarkable tendency was observed when the MWD's were compared with each other. The changes could be summarised in two series covering the two ranges of oxygen concentration (22-410 and 1000-2800 p.p.m.).

Changes in MWD's are shown in Fig. 13. High oxygen content causes a gradually increasing skewness which is pronounced after 90 min. The high molecular weight

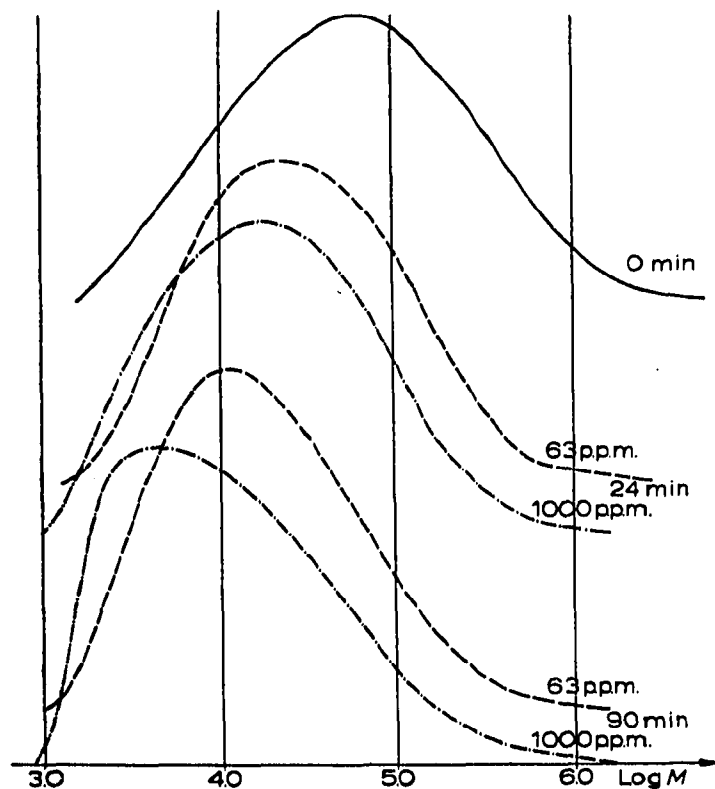


Fig. 13. Weight fraction plotted against $\log M$ (MWD) for sample A heated at 355°.

tail is still in the region of 10^6 and the low end of the MWD remains at about 10^3 . The MWD is very steep at the lower end and the peak position has moved from $\sim 10^4$ to $\sim 5 \cdot 10^3$ ($C_{700}-C_{350}$).

The reason for the difference in degradation rate between low and high oxygen concentrations is not clearly understood. A reaction that involves equilibrium conditions between oxygen and active sites for chain scission in the polymer, could be an explanation. If this is true the oxygen concentration at 410 p.p.m. should be too low for reaction whereas at 1000 p.p.m. reaction occurs. Furthermore at 1000 p.p.m. all active sites ought to be reactive and a further increase in oxygen concentration to 1900 p.p.m. should not cause any further chain scission. Work on elucidating the influence of oxygen on the chain scission is going on in our laboratory.

The curves in Figs. 11 and 12 cannot be super-imposed by sliding the time axis. Therefore it was not possible to construct an Arrhenius plot. The increase in rate at the high oxygen concentrations is 2-4 times, the lower value corresponding to the shortest heating times.

\bar{M}_w/\bar{M}_n and \bar{M}_z/\bar{M}_w values were calculated from GPC data and plotted against heating time at different oxygen levels (Fig. 14).

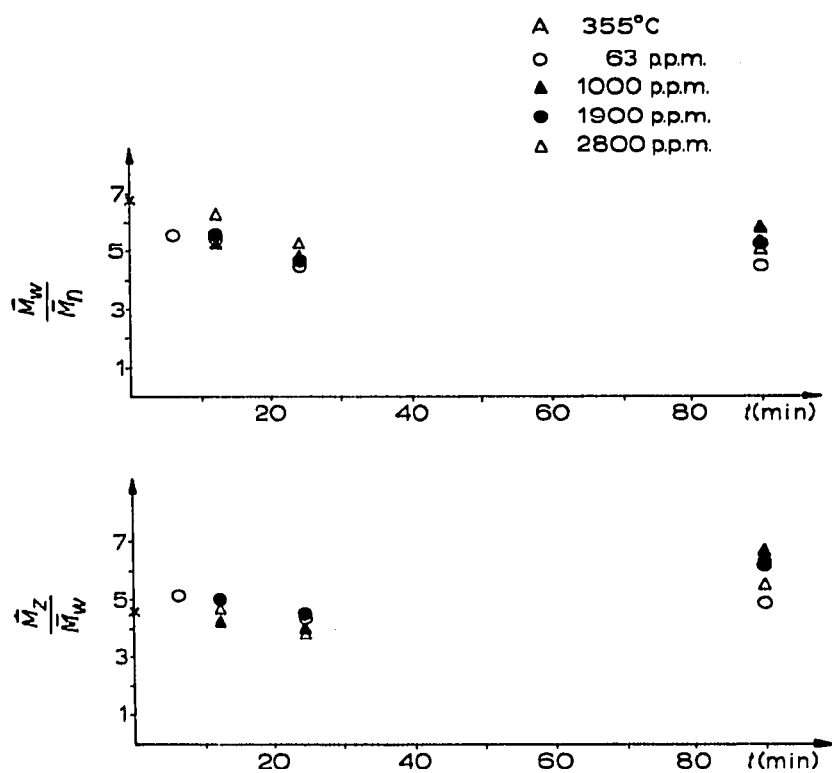


Fig. 14. \bar{M}_w/\bar{M}_n and \bar{M}_z/\bar{M}_w values for sample A, heated at 355°.

The \bar{M}_w/\bar{M}_n and \bar{M}_z/\bar{M}_w values are remarkably constant and not consistent with the drastic drop in \bar{M}_w/\bar{M}_n reported earlier, *e.g.*, by ARNETT AND STACY¹¹, for a HDPE resin. Our plots indicate a shallow minimum in the order of 4 and no continuous decrease of \bar{M}_w/\bar{M}_n approaching a value of 2, which should be expected from current theories of random scission.

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