# 619. *The Thermal Degradation of Ethylene Polymers.*

By W. G. Oakes and R. B. Richards.

The thermal degradation of ethylene polymers at temperatures above 290° has been followed by changes in average molecular weight and in the infra-red spectra. Although molecular-weight decrease is marked in the range 300—400°, ethylene or other volatile products are not formed in quantity below about 370°. In this respect the degradation is in contrast to that of styrene or methyl methacrylate polymers, which in some circumstances evolve monomer in quantity before the molecular weight of residual polymer is appreciably reduced. The shapes of the molecular weight–time curves and the changes in the concentrations of the three types of olefinic double bonds formed ($R{\cdot}CH{:}CH_2$, $R{\cdot}CH{:}CH{\cdot}R'$, and $RR'C{:}CH_2$) are interpreted in terms of a chain-reaction mechanism in which the rupture of weak links, present in very low concentration, initiates a further degradation mainly at points adjacent to branches in the polymer molecule.

Theoretical treatments of the degradation of polymers have been made by a number of authors. Calculations of the changes in average chain length and in the distribution of chain lengths have been made statistically; simple treatments based on the assumption, for example, that all bonds are equally likely to be degraded (*e.g.*, Montroll and Simha, *J. Chem. Physics*, 1940, **8**, 721) have been superseded by the more complex treatments necessary when it is postulated that there are a number of weaker links in the polymer chain (Jellinek, *Trans. Faraday Soc.*, 1944, **40**, 266; 1948, **44**, 345). A further complication in the theoretical treatments is the need to explain the very large amount of monomer produced in the thermal degradation of certain polymers such as polystyrene and poly(methyl methacrylate) (Jellinek, *loc. cit.*; Grassie and Melville, Faraday Soc. Discussion, 1947, **2**, 378). Such degradations may to some extent be regarded as reverse polymerisations, in the sense that when a molecule has started to break down, the large radical so formed loses monomer units one after the other until the whole polymer molecule has been destroyed. In such a case the average molecular weight of the residual polymer remains unchanged, even though as much as 60% of the sample has been converted into monomer [as for a poly(methyl methacrylate) sample quoted by Grassie and Melville].

Grassie and Melville point out that the extreme opposite type of degradation, by random bond breaking, leads to a large decrease in the average molecular weight of the residual polymer before an appreciable amount of monomer is produced. The thermal decomposition of polymers of ethylene at 290—400°, which is now described, approximates to this type of degradation.

*Effect of Temperature and Time of Heating on Molecular Weight.*—In the absence of oxygen, polyethylene is stable to heat at temperatures up to about 290°, but at higher temperatures the molecular weight is decreased, the products of mild degradation being plastics similar to the original polythene or hard waxes. More extensive degradation yields semi-solid pastes or liquids, but gaseous products are not formed in any appreciable quantity below about 370°, and even then ethylene is only a minor constituent of the volatile product (cf. Wall, *J. Res. Nat.*

*Bur. Stand.*, 1948, **41**, 315). In this respect polyethylene differs from styrene and methyl methacrylate polymers, which yield monomer in large quantity below 300°. The rate of decrease of molecular weight of the ethylene polymers increases rapidly as the pyrolysis temperature rises. Fig. 1 shows the changes in the intrinsic viscosity of a sample of polythene as a function of time at 315° and 360°.

From the changes in number average molecular weight (estimated from the intrinsic viscosities as described on p. 2934) in the experiments of Fig. 1, the amount of degradation was calculated in terms of the numbers of carbon–carbon links broken after various times of heating. Since every break forms one new molecule, the number $Q$ of polymer chain links broken per gram of original material is given by

$$Q = N\{1/M_t - 1/M_0\}$$

where $M_0$ and $M_t$ are the initial and final number average molecular weights and $N$ is Avogadro's number. The results are shown in Fig. 2.

The reaction rate is seen to fall away as the amount of degradation increases. If all bonds were equally likely to break, the plot of amount of degradation against time would be a straight line over the range covered in Fig. 2. The broken lines in Fig. 1 show the course of the intrinsic viscosity and time curves which would have been found if the initial rate of reaction were maintained throughout the course of the experiment.

FIG. 1.

*Effect of time of heating on intrinsic viscosity at 315° and 360°.*

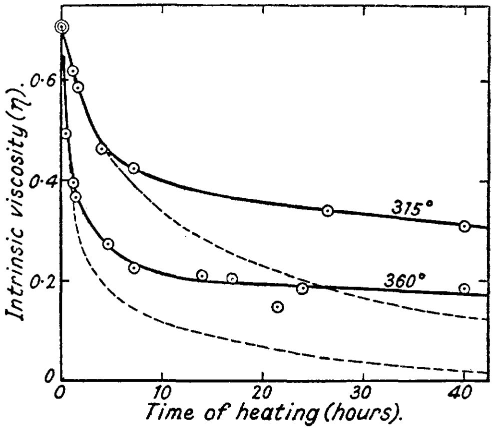
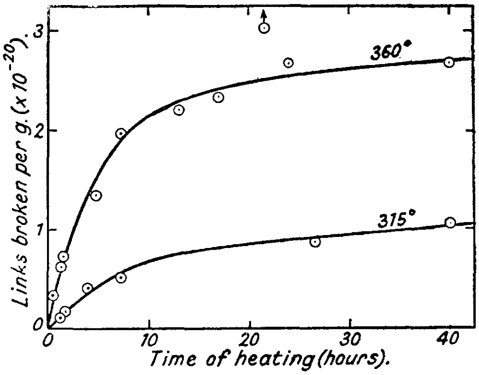


FIG. 2.

*Effect of time of heating on number of chain links broken.*



The decrease of reaction rate as the amount of degradation increases could be explained if the molecules were more stable as the chain length decreased, or if there were a number of weak links in the chains as postulated in the case of polystyrene by Jellinek. The mechanism of degradation will be discussed after the properties of the thermal degradation products have been described.

*The Chemical Structure of the Degradation Products.*—The analysis of the products of thermal degradation, like that of polythene itself, corresponds closely to the empirical formula $(CH_2)_n$, except that oxygen is detected in samples in which air or oxygen is not rigidly excluded, as, for example, in the case of samples degraded under ordinary cylinder nitrogen. The most important change, as the extent of degradation increases, is that the degree of unsaturation, as indicated, *e.g.*, by an iodine value, increases. This is shown in Table I for a series of pyrolysis products of molecular weight from 10,000 down to 220. This table also includes a figure for the average number of double bonds per molecule calculated from the iodine value (I.V.) and the number average molecular weight ($M$). This figure is seen to be close to 1·0 for the bulk of the samples and the products thus approximate closely on the average to mono-olefins at all stages of degradation. Confirmation of this is given by quantitative hydrogenation in decalin solution in the presence of Adams's platinum oxide. Results are shown in Table II.

Iodine numbers or the hydrogenation results give no indication whether the double bonds in these degradation products are of the vinyl or polysubstituted ethylene types, but evidence on this point is given by the infra-red absorption spectra.

TABLE I.

*Iodine numbers of polythene degradation products.*

| *M* (number average). | I.V. | Double bonds per molecule. | *M* (number average). | I.V. | Double bonds per molecule. |
|---|---|---|---|---|---|
| 10,000—15,000 (polythene) | 1—2 | 0·3—0·8 | 3800 | 6·9 | 1·03 |
| | | | 1870 | 11·0 | 0·81 |
| 9600 | 1·6 | 0·60 | 850 | 29·1 | 0·98 |
| 8900 | 1·8 | 0·63 | 685 | 32·1 | 0·87 |
| 6500 | 2·9 | 0·76 | 505 | 57·1 | 1·13 |
| 5800 | 4·2 | 0·96 | 365 | 81·9 | 1·18 |
| 5700 | 4·2 | 0·94 | 260 * | 95·8 | 0·98 |
| 4300 | 7·2 | 1·22 | 220 * | 129·7 | 1·12 |

* These samples were obtained from the samples of molecular weight 365 by vacuum distillation.

TABLE II.

*Hydrogen uptake of polythene degradation products.*

| | | | |
|---|---|---|---|
| *M* (number average) | 4000 | 1870 | 1050 |
| $H_2$ uptake (c.c. at N.T.P. per g.) | 4·5 | 13·0 | 25·6 |
| Double bonds per molecule | 0·8 | 1·1 | 1·2 |

A number of the samples made during the early stages of this work has been examined by Thompson and Torkington (*Proc. Roy. Soc.*, 1945, *A*, **184**, 1) and the spectra of further samples have been measured in this laboratory. The main change in the infra-red spectrum as the extent of pyrolysis is increased (by increasing the pyrolysis temperature rather than by increasing the reaction time) is that the intensity of bands in the 10—12 μ. region (800—1000 cm.$^{-1}$) increases markedly. The bands found in pyrolysed polythene are shown in Table III.

TABLE III.

*Infra-red bands for unsaturated groups found in pyrolysed polythene.*

| | | | | |
|---|---|---|---|---|
| Frequency, cm.$^{-1}$ | 908 | 990 | 964 | 887 |
| Wave-length, μ | 11·0 | 10·1 | 10·35 | 11·3 |
| Double-bond type | $\mathrm{R{\cdot}CH{:}CH_2}$ | | $\mathrm{R{\cdot}CH{:}CHR'}$ | $\mathrm{RR'C{:}CH_2}$ |

Although a band at 835 cm.$^{-1}$ corresponding to the trialkylethylene type of double bond, $\mathrm{RR'C{:}CHR''}$, has been found in low intensity in one or two polythene samples, it does not appear to be formed by pyrolysis. A band at about 700 cm.$^{-1}$ found in *cis*-pent-2-ene and possibly characteristic of the *cis*-1 : 2-dialkylethylene group, $\mathrm{R{\cdot}CH{:}CHR'}$, has not been observed in pyrolysed polythene. By comparing the intensities of absorption at the above frequencies, it is possible to follow the production of the various types of double bonds as the extent of degradation increases. Extinction coefficients for the bands shown in Table III in semi-solid long-chain polymers are not yet known reliably. We have, however, used the average values for liquid olefins based on the work of Anderson and Seyfried (*Anal. Chem.*, 1948, **20**, 998) to estimate the relative proportions of double bonds of the types $\mathrm{RCH{:}CH_2}$, $\mathrm{RCH{:}CHR'}$, and $\mathrm{RR'C{:}CH_2}$ in the samples examined by Thompson and Torkington and in samples of even lower molecular weight examined here. Table IV shows values of log $I_0/I$ for the bands at 908, 990, 964, and 887 cm.$^{-1}$ taken from the diagrams in Thompson and Torkington's paper. It shows that as molecular weight is decreased the intensities of the bands due to the vinyl group increase relatively to the other two, and indeed as the molecular weight approaches 500 the intensities of the 887 and 964 cm.$^{-1}$ bands seem almost to have reached a steady value.

TABLE IV.

*Changes in infra-red absorption due to three types of double bond as extent of pyrolysis increases.*

| | | log $I_0/I$ for constant thickness. | | | |
|---|---|---|---|---|---|
| | No. of C–C links broken per g. ($\times 10^{-18}$). | $\mathrm{R{\cdot}CH{:}CH_2}$. | | $\mathrm{R{\cdot}CH{:}CHR'}$. | $\mathrm{RR'C{:}CH_2}$. |
| *M* of product. | | 908. | 990. | 964. | 887. |
| 13,000 (original) | 0 | <0·1 | <0·1 | <0·1 | <0·1 |
| 5,000 | 0·8 | 0·25 | 0·18 | 0·17 | 0·17 |
| 1,100 | 5·1 | 0·40 | 0·23 | 0·22 | 0·24 |
| 700 | 8·2 | 0·52 | 0·28 | 0·27 | 0·28 |
| 500 | 11·7 | 0·90 | 0·49 | 0·27 | 0·30 |

Anderson and Seyfried's coefficients being used, the vinyl group concentration in these samples and of two even more degraded samples expressed as a percentage of the total double bond concentration is shown in Table V. These results indicate that in the early stages of pyrolysis all three types of double bond are formed, but that when the molecular weight has dropped below about 1000 virtually no double bonds are formed other than those in vinyl groups.

TABLE V.

*Vinyl group concentration as percentage of total double bond concentration.*

| | | | | | | |
|---|---|---|---|---|---|---|
| *M* | 5000 | 1100 | 700 | 500 | 320 | 220 |
| $R{\cdot}CH{:}CH_2$ as % of total C:C | 36 | 39 | 41 | 54 | 62 | 72 |

TABLE VI.

*Effect of temperature on initial rate of breaking of* C–C *bonds.*

| | | | | | |
|---|---|---|---|---|---|
| Temp. | 295° | 305° | 315° | 335° | 360° |
| No. of bonds broken $\times 10^{-18}$ (per g. per hour) | 0·14 | 0·38 | 9 | 19 | 80 |

*The Reaction Mechanism.*—The intial rates of degradation at temperatures of 295°, 305°, 315°, 335°, and 360° of the polythene samples for which results are given in Figs. 1 and 2, expressed in terms of rates of degradation of carbon–carbon links, are shown in Table VI. These results correspond to an overall activation energy of 60—70 kcals., a figure similar to those found for the thermal degradation of paraffins. Jellinek (Faraday Soc. Discussion, 1947, **2**, 399; *J. Polymer Sci.*, 1949, **4**, 13) has reported a change of activation energy of depolymerisation of polyethylene at 375—436° from 46 to 66 kcals. as molecular weight is increased from 11,000 to 23,000 (using loss in weight as a measure of reaction rate). Our experience with a range of ethylene polymers of molecular weight from 9,000 to 23,000 does not, however, indicate any significant change with chain length of the activation energy of the initial stages of degradation when molecular-weight decrease is used to measure reaction rate.

It was noted above that the rate of degradation in terms of number of bonds breaking in unit time falls away as the extent of degradation increases, and that such an effect could be explained as a result either of decreased stability of molecules as molecular weight increases, or of the presence of a few weak links in the polymer chain. It is known that in the case of low-molecular-weight paraffins in the $C_{(1)}$—$C_{(6)}$ range, the thermal stability decreases as chain length increases (Egloff, "Reactions of Pure Hydrocarbons," 1937), but it is hardly to be expected that there would be any significant decrease in stability as a direct consequence of an increase in chain length from say 100 to 1000 carbon atoms. We have compared the extent of degradation of three samples of polyethylene of initial intrinsic viscosities 0·47, 0·69, and 1·12 when heated for a constant time at various temperatures up to 360°. These results indicate rather the reverse effect, the rate of rupture of C–C bonds at 330°, for example, being respectively $21{\cdot}1 \times 10^{18}$, $10{\cdot}9 \times 10^{18}$, and $4{\cdot}8 \times 10^{18}$ bonds/g./hr. for the low, medium, and high molecular-weight samples.

The alternative hypothesis that there are weak links in the polymer chain seems more probable. As to the nature of these weak links, there is as yet no definite evidence, but some indication of their concentration is given by a consideration of the molecular weight–time relations shown in Figs. 1 and 2. If we assume that the rates of rupture of weak and of normal links are proportional to the number of each type of link ($w$ and $n$) unbroken per molecule

$$-\mathrm{d}w/\mathrm{d}t = k_w w; \quad -\mathrm{d}n/\mathrm{d}t = k_n w \quad (k_w > k_n)$$

the total number of links of each type ($S = S_n + S_w$) broken after time $t$, can be expressed in terms of the original proportion $\alpha$ of weak links per molecule and the initial chain length $P_0$. For

$$S_w = \alpha P_0 - w \text{ and } S_n = (1 - \alpha)P_0 - n$$

and

$$-\ln w = k_w t - \ln \alpha P_0$$
$$-\ln n = k_n t - \ln (1 - \alpha)P_0$$

or

$$-\ln [\alpha P_0 - S_w] = k_w t - \ln \alpha P_0$$
$$-\ln [(1 - \alpha)P_0 - S_n] = k_n t - \ln (1 - \alpha)P_0$$

whence

$$S_w = \alpha P_0 (1 - e^{-k_w t})$$
$$S_n = (1 - \alpha)P_0 (1 - e^{-k_n t})$$

and the total fraction of bonds broken $S_T/P_0$ is given by

$$S_T/P_0 = (S_w + S_n)/P_0 = 1 - e^{-k_n t} + \alpha e^{-k_n t} - \alpha e^{-k_w t}$$

In the simple case when only weak links are breaking, *i.e.*, when $k_n = 0$, we have $S_T/P_0 = \alpha\ (1 - e^{-k_w t})$. The line drawn through the 315° points in Fig. 1 corresponds to the rupture of weak bonds only, the value of $\alpha$ being $2{\cdot}4 \times 10^{-4}$; this corresponds to one weak link in every four polymer molecules. It is seen that this gives a fair representation of the experimental results.

Turning now to the results at higher temperature for the same polymer as, for example, the 360° points given in Fig. 2, it is found that these cannot be explained on the basis that only the same proportion of weak links are breaking, for, if this were so, the pyrolysis would virtually cease at a value for the number of bonds broken per g. of $1{\cdot}04 \times 10^{20}$; nor can the curve satisfactorily be explained by introducing rupture of normal carbon–carbon bonds. In this case, for the relatively low extent of pyrolysis studied, we have $S_T/P_0 = \alpha\ (1 - e^{-k_w t}) + k_n t$, and whatever values of $k_w$ and $k_n$ are chosen, a good fit with the 360° points in Fig. 2 is not possible unless the value of $\alpha$ is increased. If $\alpha$ is increased to $5{\cdot}9 \times 10^{-4}$ the simple equation for the rupture of weak bonds only represents the experimental points, as shown by the broken line in Fig. 1, without the need to postulate rupture of normal carbon–carbon bonds.

If $\alpha$ is a measure of the actual proportion of weak bonds in the polymer chain, the significance of the need to increase $\alpha$ as temperature rises is that there must be more than one type of weak link in the polymer, some being stable at 315° but not at 360°. An alternative explanation which seems more probable is that pyrolysis proceeds by a chain reaction initiated by the rupture of a weak bond; the effective value of $\alpha$ is then equal to the product of the actual proportion of weak bonds $\alpha_0$ and the kinetic chain length $n_T$ at the temperature of pyrolysis; $\alpha$ can therefore increase with increase in temperature. The true proportion of weak links may therefore be even less than the figure of 1 in 4 polymer molecules calculated above.

The fact that ethylene polymers are thermally unstable at temperatures as low as 290°, whereas hexadecane is stable in the absence of catalyst at 390°, does indeed suggest that normal $CH_2$–$CH_2$ links are not the centre of pyrolysis. That there are chain links in ethylene polymers which differ from the normal paraffinic carbon–carbon link is shown by the infra-red spectrum. Examples include bonds adjacent to carbonyl or other oxygen-containing groups derived from the catalyst or from trace impurities in the monomer, or peroxide groups derived from the oxygen catalyst. Other potential weak links are those adjacent to branches in the polymer chain. Branches in the polymer chain are known to be as frequent as one for every 50 carbon atoms, or 20 per molecule of a polymer such as that to which the results of Figs. 1 and 2 relate. It is therefore improbable that these links are the weak links, the existence of which is postulated to explain the shape of the molecular weight–time curves. On the other hand, the nature of the olefinic groups produced by pyrolysis, and particularly the manner in which the proportions of the various types change as the extent of pyrolysis proceeds, suggests very strongly that branches in the polymer chain are points of weakness, and it seems possible that pyrolysis proceeds by a chain reaction starting at a peroxide or other weak link present in very low concentration and propagated mainly through the points of branching in the polymer chain. Degradation of an unbranched polymethylene chain in its simplest form yields an alkyl and a vinyl group. Thus the first products of the degradation of *n*-hexane are only $\Delta^1$-olefins (Partington and Danby, *J.*, 1948, 2226). The overall reaction may be represented as

$$\mathrm{R{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2R' \longrightarrow R{\cdot}CH{:}CH_2 + CH_3R'}$$

or if the depolymerisation occurs as a free-radical chain reaction a possible mechanism is :

$$\mathrm{R''{-} + R{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2R' \longrightarrow R''H + R{\cdot}\underset{|}{C}H{\cdot}CH_2{\cdot}CH_2R'}$$
$$\mathrm{R{\cdot}\underset{|}{C}H{\cdot}CH_2{\cdot}CH_2R' \longrightarrow R{\cdot}CH{:}CH_2 + R'{\cdot}CH_2{-}}$$

and $R'{\cdot}CH_2{-}$ continues the reaction chain by removing a hydrogen atom from another polymer molecule, forming $R'{\cdot}CH_3$. Depolymerisation at a branch can, on the other hand, yield double bonds of the three types $R{\cdot}CH{:}CH_2$, $R{\cdot}CH{:}CH{\cdot}R'$, or $RR'C{:}CH_2$, a possible chain-reaction mechanism being

$$\mathrm{R'''{-} + RR'CH{\cdot}CH_2{\cdot}CH_2R'' \longrightarrow R'''H + RR'CH{\cdot}\underset{|}{C}H{\cdot}CH_2R''}$$

followed by

$$\mathrm{RR'CH{\cdot}\underset{|}{C}H{\cdot}CH_2R'' \longrightarrow RR'CH{\cdot}CH{:}CH_2 + R''{-}}$$

or

$$\mathrm{RR'CH{\cdot}\underset{|}{C}H{\cdot}CH_2R'' \longrightarrow R{\cdot}CH{:}CH{\cdot}CH_2R'' + R'{-}}$$

or, if hydrogen is removed from the tertiary carbon atom :

$$\mathrm{RR'\underset{|}{C}{\cdot}CH_2{\cdot}CH_2R'' \longrightarrow RR'C{:}CH_2 + R''{\cdot}CH_2{-}}$$

If the removal of a hydrogen atom by free radical from the polymer molecule at or adjacent to the tertiary carbon atom at a branch occurs more readily than from a length of unbranched methylene groups, then in the early stages of depolymerisation all three types of double bond ($R\cdot CH{:}CH_2$, $R\cdot CH{:}CH\cdot R'$, $RR'C{:}CH_2$) will be formed, while in the later stages, when cracking is occurring only at unbranched lengths of chain, only vinyl groups will be produced. This is the effect indicated by the infra-red absorption results.

There is evidence from work on the oxidation of hydrocarbons, including polythene, that the hydrogen atoms on the tertiary carbon atoms are more readily removed than on the methylene groups, and Rice and Rice (" The Aliphatic Free Radicals," 1937) interpreted the cracking of low-molecular-weight paraffins in terms of free-radical chain reactions involving removal of hydrogen atoms from tertiary carbon atoms. At 300°, for example, they calculate that the probabilities of hydrogen removal from primary, secondary, and tertiary carbon atoms are in the ratio 1 : 3 : 33. A comparison of the pyrolysis of two ethylene polymers of similar molecular weight synthesised under conditions which give in the one case an unusually straight-chain and in the other an unusually branched-chain polymer supports this view (Table VII).

TABLE VII.

*Pyrolysis of straight- and branched-chain polymers.*

| Pyrolysis conditions : | 2 hrs. at 330°. | | 2 hrs. at 360°. | |
|---|---|---|---|---|
| Sample. | A. | B. | A. | B. |
| Chain branching. | Low. | High. | Low. | High. |
| C–C links broken per g. ($\times 10^{-20}$) | 0·38 | 0·64 | 1·06 | 1·67 |
| Total double-bond content after pyrolysis (% of C=C by infra-red) | 0·132 | 0·182 | 0·304 | 0·420 |
| Vinyl group content (% of C=C by infra-red) | 0·062 | 0·072 | 0·160 | 0·180 |
| Vinyl as % of total double-bond content | 47 | 39 | 53 | 43 |

Sample A : $[\eta] = 0{\cdot}695$, $d^{20} = 0{\cdot}953$, $CH_3/CH_2$ ratio = *ca.* 1 : 100.
Sample B : $[\eta] = 0{\cdot}725$, $d^{20} = 0{\cdot}916$, $CH_3/CH_2$ ratio = *ca.* 1 : 40.

These results show that the polymer with the less branched chain produces the higher proportion of vinyl group, and that, as in Thompson and Torkington's results analysed in Table IV, the proportion of vinyl groups increases as the degree of degradation increases.

A further point to support the hypothesis that the tertiary carbon atoms are weak points in the polymer chain is the approximate correspondence between the average length of chain between branches in normal polythene (about 70 carbon atoms) and the chain length below which further degradation produces vinyl groups but not $R\cdot CH{:}CHR'$ or $RR'C{:}CH_2$ groups (Table IV).

## EXPERIMENTAL.

In the experiments, the results of which are given in Figs. 1 and 2, samples of about 5—10 g. of polythene were heated for the appropriate time in glass tubes in copper block furnaces controlled to better than $\pm\frac{1}{2}$°. The tubes were in some cases evacuated continuously but in one or two cases they were filled with oxygen-free nitrogen. No difference was observed between the rate of degradation in the nitrogen-filled or the evacuated tubes. For the preparation of larger samples used, for example, for the hydrogenation, the infra-red, and the iodine number work, polythene was depolymerised in a small continuous apparatus. Molten polythene was forced by nitrogen pressure at a controlled rate through a 1-cm. Pyrex-glass tube in a tubular furnace.

Intrinsic viscosities of the samples were measured in tetralin at 75°. In a number of cases number average molecular weights were determined from the b. p. elevation of benzene, an apparatus of the Menzies and Wright type being used. This was found to give results reproducible to ±5% for samples of molecular weight up to 3000, and approximate results up to molecular weights of 6000 were obtained. A plot of intrinsic viscosity against number average molecular weight for the degraded polythenes, supplemented by data from osmotic-pressure measurements on undegraded polythene, although not a single line (because of variations in molecular-weight distribution and chain branching) was a band narrow enough to make possible the estimation of number average molecular weights from the rapid and convenient intrinsic viscosity measurements. The relation $[\eta] = 1{\cdot}08M^{0\cdot7} \times 10^{-3}$ gave number average molecular weights which were considered reliable enough for the calculations of rate of degradation used above.

Iodine numbers were determined by a modification of the Wijs method. The sample was dissolved in about 10 times its weight of carbon tetrachloride and on cooling formed a finely divided gelatinous precipitate which was treated with iodine monochloride solution in glacial acetic acid in the dark for 3 hours, residual iodine monochloride being determined as usual. In the case of the lower molecular-weight samples with iodine numbers of 10 or greater, reproducibility was satisfactory. It has since been shown that some substitution occurs with these samples and the iodine values, and hence the figures for double bonds per molecule given in Table I, may be up to 10% too high.

Hydrogenation results were obtained in apparatus similar to that described by Jackson and Jones (*J.*, 1936, 895), using as catalyst, Adams's platinic oxide made as described in *Org. Synth.*, Coll.

Vol. I, p. 452. Decalin was used as solvent, and the hydrogenation was done at about 60°. Here again results were fairly satisfactory for the lower molecular-weight waxes where the hydrogen absorption was of the order of 10—20 c.c. per g., but it was very slow, up to 24 hours being necessary to obtain a constant figure.

Infra-red absorption spectra (except those determined by Thompson and Torkington) were measured in this laboratory by Mr. L. H. Cross, using a Grubb Parsons single-beam recording instrument.

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IMPERIAL CHEMICAL INDUSTRIES RESEARCH DEPARTMENT,
ALKALI DIVISION, NORTHWICH.

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