On the Thermal Degradation of Poly(vinyl Chloride). II. The Effect of Atmosphere

KENT B. ABBÅS* and ERLING M. SÖRVIK, *The Polymer Group, Department of Organic Chemistry, Chalmers Unisersity of Technology and University of Gothenburg, Göteborg 5, Sweden*

Synopsis

The early stages of the thermal degradation of PVC were studied. Two commercial, suspension-polymerized resins were thermally treated at different temperatures and oxygen contents. Dehydrochlorination kinetics were followed by conductometric measurements and the formation of polyene sequences by ultraviolet-visible spectroscopy. Crosslinking and chain scission were followed by gel chromatography (GPC) and viscometry. No chain scission was observed in nitrogen atmosphere and no crosslinking in oxygen. Degradation in air proceeded by both reactions. The rate of dehydrochlorination for one of the investigated polymers increased linearly with the logarithm of the oxygen pressure. In nitrogen, an increasing degradation temperature was found to give both an increasing crosslinking and less discoloration. In oxygen, chain scission reactions showed a slight temperature dependence. The temperature effect on the discolorations was similar to that in nitrogen. The main difference between the investigated resins was the amount of internal double bonds in the original polymers, the ratio being 2:1. The higher amount resulted in a higher rate of dehydrochlorination, a larger extent of chain scission in oxygen, and a lower extent of crosslinking in nitrogen. Both in oxygen and nitrogen, the obtained results are consistent with allylic mechanisms. In nitrogen, the polyene formation supposedly proceeds by a unimolecular reaction and crosslinking by an intermolecular nonradical dehydrochlorination. In oxygen, radical reactions are superposed and may lead to chain rupture via β-scissions of alkoxy radicals.

INTRODUCTION

Although the thermal degradation of PVC has been extensively studied, few detailed investigations have been published on the thermal degradation in oxygen. It is, however, generally accepted that the presence of oxygen will cause (1) a faster dehydrochlorination,[1-11] (2) a less intense discoloration due to shorter polyene sequences,[3,6,8,11-15] and (3) chain scission reactions.[1,3,6,16-19]

Very few quantitative measurements of the thermal degradation of PVC in the presence of oxygen have been published.[1,16] Druesedow and Gibbs[1] studied the thermal degradation in air. At 190°C, they found a small decrease in the intrinsic viscosity followed by an increase. At 200°C, both effects were more pronounced. Arlman[16] measured the changes in

*Earlier publications under the family name Andersson.

the viscosity standard value (*VSV*) during degradation at 182°C. The viscosity increased continuously when degradation took place in nitrogen. In oxygen, the *VSV* initially dropped, but then became constant. Degradation in air showed only a very slight viscosity decrease. Insoluble material appeared earlier the higher the oxygen content in the degradation atmosphere.

Although some air is always present during PVC processing, no investigation has been published so far concerning the thermal degradation of PVC at low oxygen pressures. Arlman[16] found that the rate of dehydrochlorination increased continuously with the oxygen content in the carrier gas. Eight concentrations of oxygen, including "pure" nitrogen and oxygen, were tested at 182°C. With the exception of nitrogen, no oxygen concentration lower than 21% (air) was used. Talamini and Pezzin[5] studied the effect of oxygen (2–100%) on the thermal degradation of PVC. The investigation was carried out, however, at 230°C and to very high conversions.

Owing to the lack of published data within this field, we decided to investigate the early stages of thermal degradation of PVC at low oxygen pressures. The changes in molcular structure was followed up by measurements of dehydrochlorination, viscosity, molecular weight distribution, and formation of polyene sequences.

EXPERIMENTAL

Materials

Suspension-polymerized PVC samples were generously supplied by KemaNord AB, Sweden. Data of investigated polymers are collected in Table I. Pevikon R-341 was precipitated before use: 20 g PVC was dissolved in peroxide-free, freshly distilled tetrahydrofuran (THF), and the solution was kept under inert atmosphere for more than 24 hr. It was then poured into a large amount of methanol (puriss). The precipitate was filtered off and carefully washed with methanol before it was left to dry in air. The resulting powder was crushed and sieved. A particle fraction between 0.200 and 0.315 mm was used for the degradation experiments. As the precipitation of Pevikon R-341 did not change its rate of dehydrochlorination, Pevikon R-45 was used without purification.

TABLE I
Data of Investigated Polymers

Polymer	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	CH₃ per 1000 C[a]	Internal double bonds per 1000 C
Pevikon R-341	48,000	114,000	2.4	5.4	0.027
Pevikon R-45	49,000	113,000	2.4	5.1	0.054

[a] Determined according to ASTM D 2238-64 T, 1964.

Tetrahydrofuran was refluxed over sodium borhydride until no peroxides could be detected.[20] It was then distilled under nitrogen from metallic sodium.

Besides air and pure oxygen, the following mixtures of oxygen in nitrogen were used: 3.4, 90, 1450, 4300, 7400, 19,700, and 70,000 ppm (by volume). All gases were supplied and analyzed by AGA, Sweden. The lowest oxygen content, 3.4 ppm, corresponds to "extra pure" nitrogen. Such a low oxygen concentration will, however, be possible to be maintained only in completely closed systems containing no rubber tubing. A more realistic figure in our case is 10 ppm oxygen.

Dehydrochlorination Kinetics

A description of the dehydrochlorination apparatus has been given earlier.[21]

Ultraviolet-Visible Spectroscopy

Transmission spectra of PVC solutions in THF were obtained by a Beckman DK-2A spectrophotometer. All PVC solutions (4 g/l.) were carefully prepared under inert atmosphere and were rotated in sealed glass tubes for 4–6 hr before analysis. The THF has to be free from peroxides and was therefore treated as mentioned above (see Materials).

Viscometry

Viscosities were measured at 25°C using Cannon-Ubbelohde viscometers adapted for dilution.[22] Kinetic energy corrections[23] were applied to all determinations. The PVC samples were dissolved in peroxide-free THF under nitrogen. The solutions were kept in darkness for 24 hr and then heated in autoclaves for 2 hr at 120°C. After cooling, they were filtered under pressure through a Kreuger asbestos filter (1 μm). The intrinsic viscosities were obtained in a concentration range of 2–5 g/l. Each sample was measured at least twice.

Gel Permeation Chromatography

A Waters Associates GPC Model 200 equipped with an automatic injection system was used for determination of molecular weight distributions. The experimental conditions were as follows: solvent, peroxide free THF; temperature, 25°C; columns, 10^7, 10^5, 5×10^4, 10^4, and 10^3 Å; sample concentration, 2 mg/ml; flow rate, 1 ml/min; plate count, 975 plates/ft. The column combination was calibrated with polystyrene standards with narrow distributions (Waters Associates, Inc., Framingham, Mass., U.S.A.).

The concept of universal calibration proposed by Benoit et al.[24] was used. The intrinsic viscosities of the polystyrene standards were measured in THF at 25°C. The obtained values showed noticeable differences from common Kuhn-Mark-Houwink relationships only at very low

molecular weights. To transform the universal calibration to PVC cali-
bration, a relationship proposed by Bohdanecký et al., [25]

$$[\eta] = 1.50 \times 10^{-4} \, \bar{M}_w{}^{0.77} \; dl/g$$

was used. In this equation, the intrinsic viscosity values were corrected
for polydispersity.

Molecular weights and molecular weight distributions were calculated
by a computer program devised by Drott and Mendelson.[26] This program
can also be used for the calculation of the degree of long-chain branching
(LCB) if GPC data are combined with intrinsic viscosity measurements.
Owing to the small amount of sample, such measurements were not pos-
sible to be carried out throughout this investigation. The LCB was there-
fore not determined quantitatively and the MWD's were not corrected
for LCB. This will result in an underestimation of molecular enlargements
and the calculated molecular weights ($\bar{M}_w$). Anyhow, the MWD's in
combination with the calculated molecular weight averages give a good
semiquantitative measure of the molecular changes during the thermal
degradation of PVC (cf. p. 3584). In connection with a detailed study of
the molecular enlargement reactions, quantitative measurements on LCB
will soon be reported.

Besides LCB, the hydrodynamic volume is also affected by the presence
of conjugated double bonds in the degraded PVC molecules. According
to a recent investigation, the intrinsic viscosity will decrease with increas-
ing degree of dehydrochlorination and pass through a minimum.[27] At the
low degrees of dehydrochlorination actual in our work, the effect of double
bonds will be negligible.

Determination of Internal Unsaturation

When a suspension of swelled PVC is treated with ozone in the presence
of methanol for a sufficiently long time, the polymer chains will be broken
at existing double bonds.[28,29] From measurements of the number-average
molecular weight before and after such a treatment, the amount of internal
double bonds (IDB) can be calculated:

$$IDB/2000C = [(1/DP) - (1/DP_0)] \cdot 10^3$$

where DP is the number-average degree of polymerization after ozoniza-
tion and DP_0 is the original number-average degree of polymerization.
Molecular weights have been determined by GPC. The ozonization was
carried out as follows: About 2 g PVC was suspended in 150 ml chloroform
and was left to swell for 15–30 hr. Before the ozonization, a few drops of
methanol were added. Ozone was generated by leading oxygen (6 l./hr)
through an ozonator (Model T-23, Projecting AB, Stockholm). The gas
was bubbled through the PVC suspension for 3 hr; no further decrease in
the molecular weight was observed after 2 hr. After ozonization, the
polymer suspension was poured into 300 ml methanol. When the polymer

was settled, the excess of liquid was sucked off and the remaining fluid was evaporated in air.   Finally, the polymer was dried at 50°C for about 20 hr.

RESULTS

In the following, the degree of dehydrochlorination or the conversion, $x\%$, is defined as the ratio of hydrogen chloride evolved to the totally available amount.   The rate of dehydrochlorination is designated as r and expressed in $(\%) \cdot min^{-1}$.   The effect of different oxygen pressures on the rate of dehydrochlorination at 180°C is demonstrated for Pevikon R-341 in Figure 1.   At 'volume fractions of oxygen lower than 1450 ppm, the degradation rate was independent of the oxygen content within experimental error.   At 7400 ppm oxygen, however, a distinct increase was observed.   In air, the measured rate was about 35% higher than in pure nitrogen.   In Figure 2, the rate of dehydrochlorination is plotted as a function of the partial pressure of oxygen in the carrier gas.   Pevikon R-341 was investigated at 180°, 190°, and 200°C, and Pevikon R-45, at 190°C.

Linear relationships between the rate of dehydrochlorination and the square root of the partial oxygen pressure have been reported by Talamini and Pezzin[5] and by Carstensen.[30]   As a matter of fact, even Arlman's results[16] will fit such a relationship quite well, although they were not presented in that way.   Our data, however, do not obey a square-root dependence, but show a linear dependence of the degradation rate on the logarithm of the oxygen pressure ($p_{O_2} > 0.005$ atm).   An exception to this
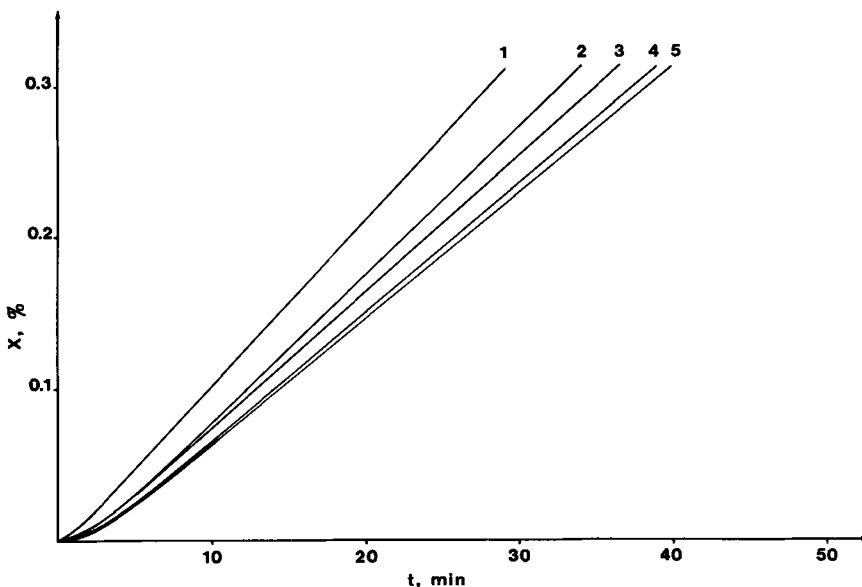

Fig. 1. Conversion x as a function of degradation time for Pevikon R-341 at 180°C in the presence of (1) oxygen, (2) air, (3) 19,700 ppm oxygen, (4) 7400 ppm oxygen, and (5) 1450–10 ppm oxygen.

TABLE II
Values of k and a in Eq. (1)

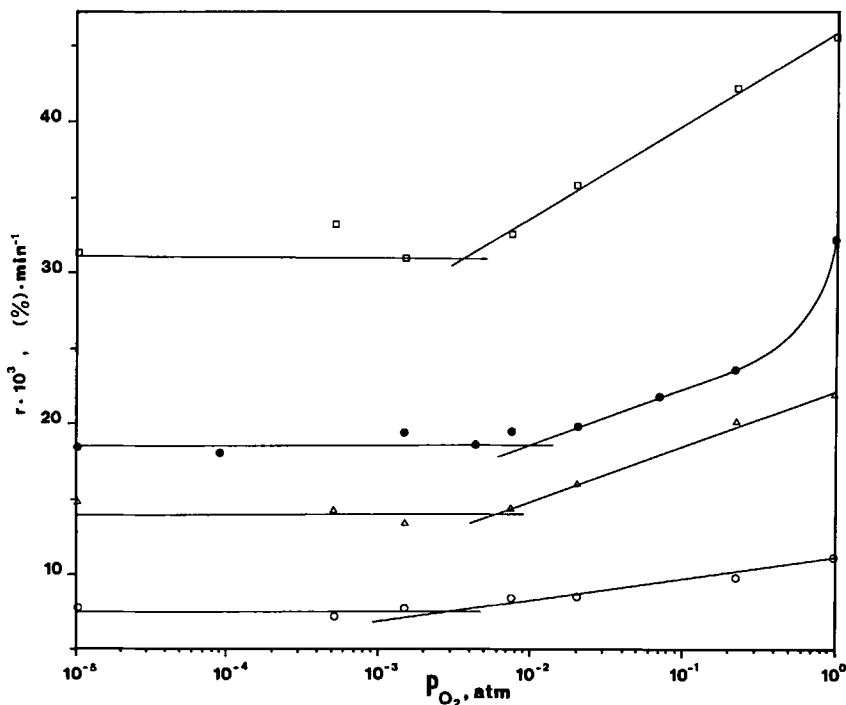| Temp, °C	$k \times 10^6$, sec^{-1}	$a \times 10^6$, sec^{-1}
180	0.218	1.800
190	0.602	3.687
200	1.017	7.645

Fig. 2. Rate of dehydrochlorination r as a function of partial oxygen pressure: (●) Pevikon R-45 degraded at 190°C; (O) Pevikon R-341 degraded at 180°C; (Δ) 190°C, and (□) 200°C.

is the result obtained for Pevikon R-45. In the range between 0.5% and 21% oxygen content, it is possible to fit the data equally well to a square-root dependence or to the straight-line dependence characteristic for Pevikon R-341. In pure oxygen, however, Pevikon R-45 showed an unexpectedly high dehydrochlorination rate (obtained as the mean value of four measurements). For Pevikon R-341, the rate of dehydrochlorination, r, between 0.5% and 100% oxygen can be expressed as follows:

$$r = k \cdot \log p_{O_2} + a \qquad (1)$$

where k and a are temperature-dependent parameters and p_{O_2} is the volume fraction of oxygen in the carrier gas. The values of k and a at different temperatures are shown in Table II.
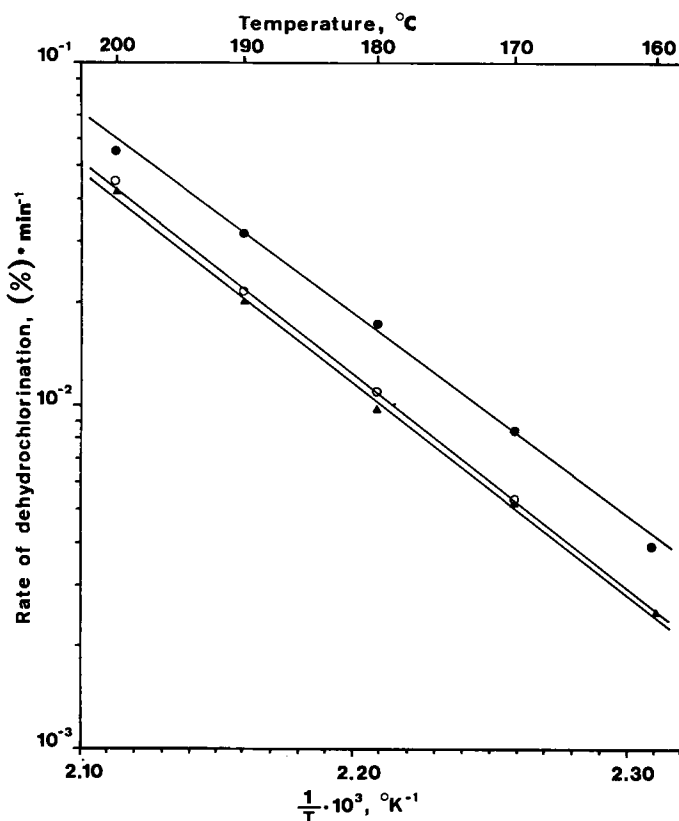
Fig. 3. Arrhenius plots for Pevikon R-45 degraded in oxygen (●); Pevikon R-341 degraded in oxygen (O) and in air (▲).

Due to the high sensitivity of the dehydrochlorination apparatus, the dehydrochlorination rates can be measured with high accuracy already at very low conversions. The calculated activation energies will therefore characterize the initial degradation processes. Arrhenius plots for PVC degraded in oxygen and air are shown in Figure 3. The activation energies for Pevikon R-341 in the presence of 1450 ppm oxygen or more were calculated to be 28.4 ± 0.4 kcal/mole. The corresponding value in nitrogen was found to be 27.9 ± 1.5 kcal/mole.[21] For Pevikon R-45, the activation energies in oxygen and nitrogen were 26.9 ± 0.9 and 26.2 ± 0.6 kcal/mole,[21] respectively. The obtained values are well within the range of earlier data.[21] Contrary to most of these, however, no significant difference was found between the activation energies in oxygen and nitrogen.

Ultraviolet-visible spectra for Pevikon R-341 were determined at 0.3% conversion. At 170–190°C, only slight differences were observed for oxygen contents below 1.97%. At 200°C (Fig. 4), the spectrum obtained at 1.97% significantly deviates from those at lower oxygen concentrations.

A commencing deterioration of details of the ultraviolet-visible spectra due to the effect of oxygen was observed already at 1.97% oxygen. From degradation tests in nitrogen at different temperatures, the spectra shown in Figure 5 were recorded. As can be seen, a temperature increase will lower the fraction of long polyene sequences, and thus the discoloration. This temperature effect was also observed in air, and is demonstrated in Figure 6.

The molecular weight changes during thermal degradation of PVC have usually been explained by chain scission or crosslinking, the latter leading to branching or network structures. The effects of a simultaneous crosslinking and chain scission are hard to investigate, but the use of GPC facilitates such measurements.
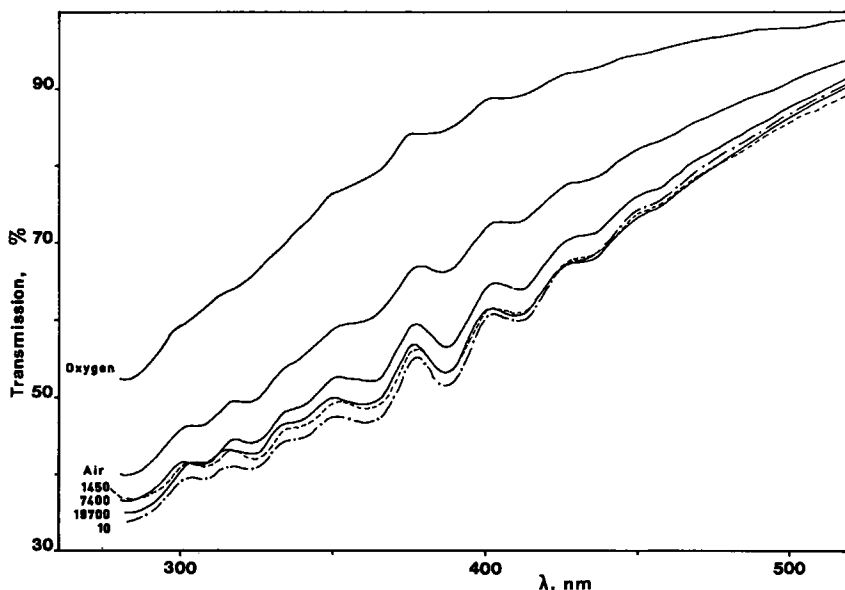

Fig. 4. Ultraviolet-visible spectra for Pevikon R-341 degraded at 200°C to 0.3% conversion. Effect of different oxygen content in the carrier gas.

A chain scission process shifts the MWD to lower molecular weights. A molecular enlargement will be observed as an increase of the high molecular weight tail. Simultaneous chain scission and crosslinking cause a combination of the above-mentioned effects. In the following, the type of structural changes is stated. A semiquantitative measure of these changes is given by comparing the molecular weight averages. Molecular weight averages for Pevikon R-341 degraded to 0.3% conversion at different oxygen content and at varying temperatures are collected in Tables III and IV. When the oxygen content was limited to less than 1.97%, a molecular weight increase was observed. This increase was larger the lower the oxygen content and the higher the degradation temperature.

During thermal degradation in air, a slight decrease in molecular weight was generally observed. This drop was further pronounced in pure oxygen. These results are consistent with the viscosity measurements reported by Arlman.[16]
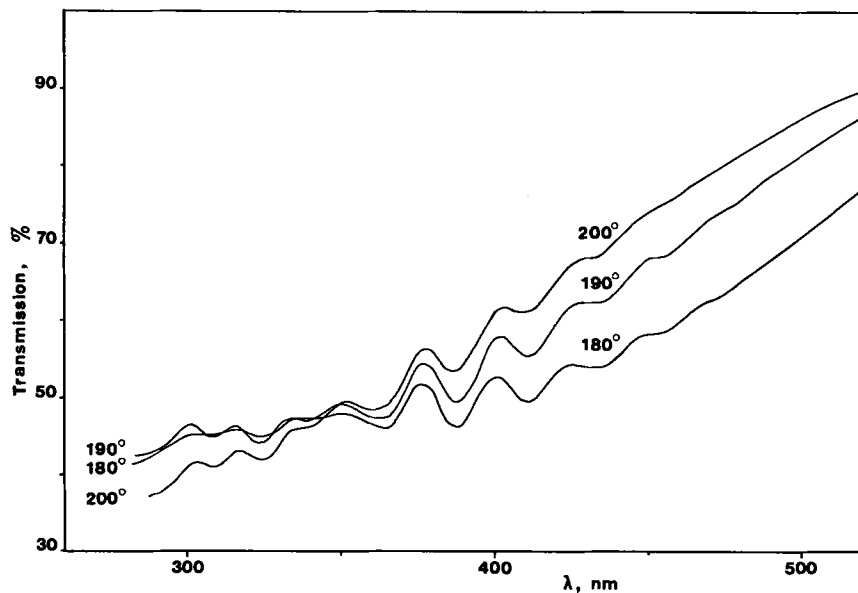

Fig. 5. Ultraviolet-visible spectra for Pevikon R-341 degraded in nitrogen to 0.3% conversion. Effect of degradation temperature.
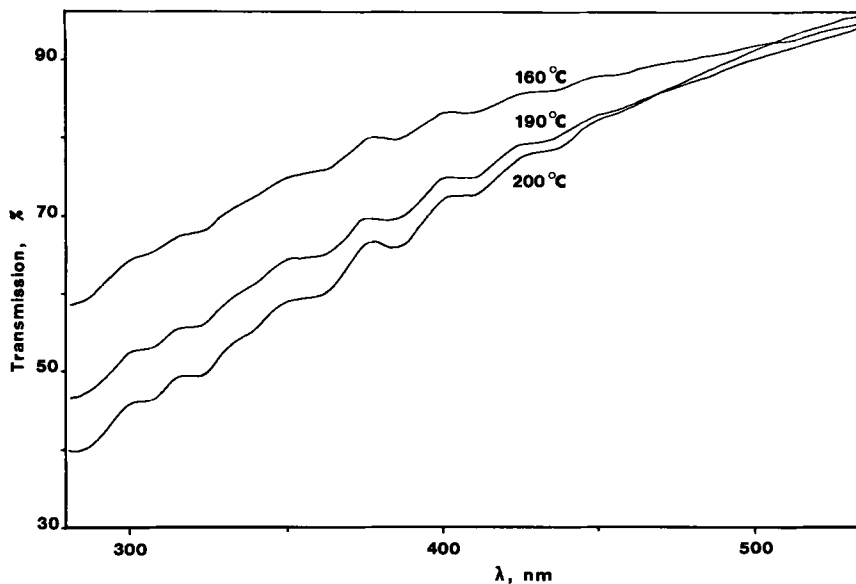

Fig. 6. Ultraviolet-visible syectra for Pevikon R-341 degraded in air to 0.3% conversion. Effect of degradation temperature.

TABLE III
Molecular Weight Averages Calculated for Pevikon R-341 Degraded to
0.3% Dehydrochlorination.   Effect of Degradation Temperature at
Constant Oxygen Content

Temp., °C	Oxygen content, %	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
170	0.001	51,000	136,900	2.7
180	0.001	50,200	131,400	2.6
190	0.001	51,800	154,300	3.0
200	0.001	51,200	156,700	3.1
180	0.145	49,100	125,600	2.6
190	0.145	51,200	134,200	2.6
200	0.145	48,900	141,500	2.9
180	0.74	49,500	125,700	2.5
190	0.74	48,800	111,100	2.3[a]
200	0.74	49,000	131,800	2.7
180	1.97	49,700	119,600	2.4
190	1.97	47,400	119,100	2.5
200	1.97	48,400	114,600	2.4
160	21	44,600	113,600	2.6
180	21	45,900	118,800	2.6
190	21	49,200	112,100	2.3
200	21	46,500	113,500	2.5
170	100	45,000	103,700	2.3
180	100	45,600	106,900	2.3
190	100	43,100	102,100	2.4
200	100	42,700	101,000	2.4

[a] Calculated from a somewhat distorted GPC chromatogram.

TABLE IV
Molecular Weight Averages Calculated for Pevikon R-341 Degraded to 0.3%
Dehydrochlorination.   Effect of Oxygen Content at
Constant Degradation Temperature

Temp., °C	Oxygen content, %	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
180	100	45,600	106,900	2.3
180	21	45,900	118,800	2.6
180	1.97	49,700	119,600	2.4
180	0.74	49,500	125,700	2.5
180	0.145	49,100	125,600	2.6
180	0.001	50,200	131,400	2.6
190	100	43,100	102,100	2.4
190	21	49,200	112,100	2.3
190	1.97	47,400	119,100	2.5
190	0.74	48,800	111,100	2.3[a]
190	0.145	51,200	134,200	2.6
190	0.001	51,800	154,300	3.0
200	100	42,700	101,000	2.4
200	21	46,500	113,500	2.5
200	1.97	48,400	114,600	2.4
200	0.74	49,000	131,800	2.7
200	0.145	48,900	141,500	2.9
200	0.001	51,200	156,700	3.1

[a] Calculated from a somewhat distorted GPC chromatogram.
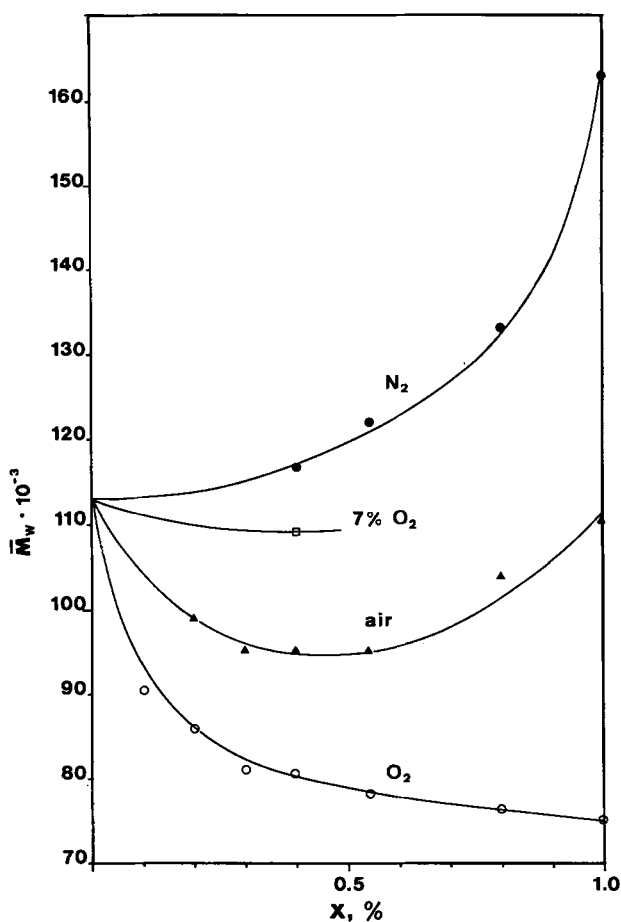
Fig. 7. $\bar{M}_w$ as a function of conversion x. Data for Pevikon R-45 degraded at 190°C at different oxygen levels.

In oxygen, an increase in temperature seemed to give a larger decrease in molecular weight, but in air no such temperature dependence could be detected. As later demonstrated for Pevikon R-45 (Figs. 8 and 9), molecular weight distributions showed no tendency to chain scission reactions during degradation in nitrogen, and no tendency of crosslinking was found during degradation in oxygen. In air, however, both chain scission and crosslinking occur. After low conversions (0.3%), only slight changes in the molecular weight distributions were noticed. A tendency to higher heterogeneity indices, $\bar{M}_w/\bar{M}_n$, are, however, observed.

The molecular weight changes during thermal degradation of Pevikon R-45 at 190°C and different oxygen levels are shown in Figure 7. As can be seen, chain scission is more pronounced in this case than for Pevikon R-341 (Tables III and IV). On the other hand, crosslinking is less extensive. At 7.0%, oxygen chain scission similar to that of Pevikon R-341 in

air was found. It is obvious that during the degradation of Pevikon R-45 in air, the effect of chain scission predominates up to about 0.5% conversion, but then crosslinking dominates. Thus, at 1.0% conversion, $\bar{M}_w$ will be about the same as that of the original polymer.

The competition between crosslinking and chain scission is illustrated by Figure 8. The original molecular weight distribution (MWD) of Pevikon R-45 is shown together with the MWD of a sample degraded in air at 190°C up to 1.0% conversion. Chain scission has shifted the distribution to lower molecular weights, but the subsequent crosslinking has increased the high molecular weight end of the distribution. The MWD's
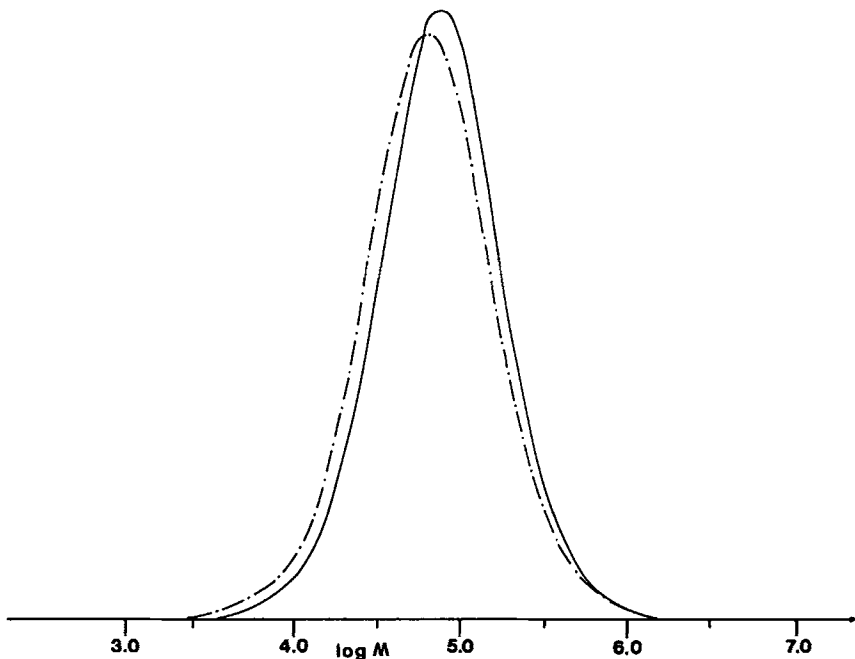
Fig. 8. Molecular weight distributions of Pevikon R-45 (———) and Pevikon R-45 thermally degraded in air at 190°C to 1.0% conversion (—·—).

for Pevikon R-45 degraded in oxygen, air, and nitrogen at 190°C to 0.8% conversion are compared in Figure 9. A comparison with the original MWD shows that no crosslinking occurs during degradation in oxygen. No increase of the high molecular weight fraction could be detected even at 1.5% conversion. No chain scission was observed during the degradation in nitrogen.

As a comparison, intrinsic viscosity measurements were carried out on Pevikon R-45. They are shown in Figure 10. The results agree with those obtained by GPC.

In Figure 11, the number of scissions per monomer unit were plotted as a function of conversion. Data are shown for Pevikon R-45 degraded in air
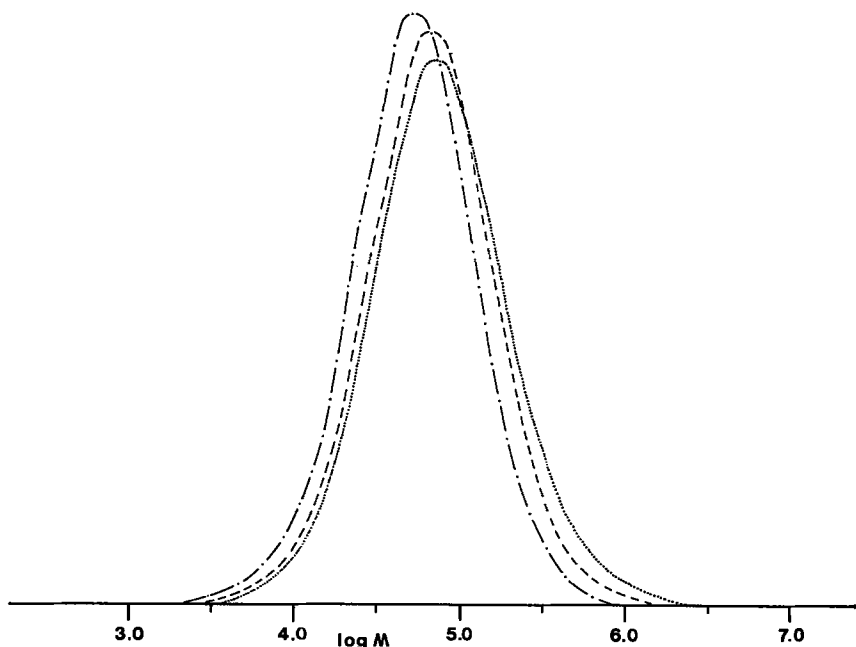
Fig. 9. Molecular weight distributions of Pevikon R-45 thermally degraded at 190°C to 0.8% conversion in nitrogen (······), in air (— — —), and in oxygen (—·—).

and oxygen at 190°C. In both cases, the reaction rate decreases with the extent of degradation.

DISCUSSION

A number of initiation sites for the dehydrochlorination of PVC have been suggested.[31,32] Investigations on model compounds have shown that allylic chlorine and, secondly, tertiary chlorine at branch points are the most plausible initiation sites.[31-34] For the formation of polyene structures in non-oxygen atmospheres, several mechanisms have been proposed: radical mechanisms,[2,18,31,32,35-37] ionic,[8,18,31,32,38] and a unimolecular mechanism.[1,3,8,19,31,32] Radical mechanisms seem to be fairly hard to verify experimentally, while a unimolecular mechanism is in accordance with recent investigations[11,32,39]:

$$—\overset{\delta^{\oplus}}{\underset{\underset{H}{|}}{CH}}—\overset{}{\underset{\underset{\delta^{\ominus}}{\underset{|}{Cl}}}{CH}}— \rightarrow —\overset{\delta^{\ominus}}{\underset{\underset{\delta^{\oplus}}{\underset{|}{H}}}{CH}}—\overset{\delta^{\oplus}}{\underset{\underset{\delta^{\ominus}}{\cdots\underset{|}{Cl}}}{CH}}— \rightarrow —CH{=}CH— + \overset{\cdot}{H}Cl \qquad (1)$$
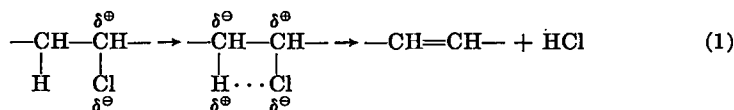
Our results (Fig. 9) show that there is no tendency to chain scission in nitrogen. Crosslinking resulting in an increased branching is, however, ob-
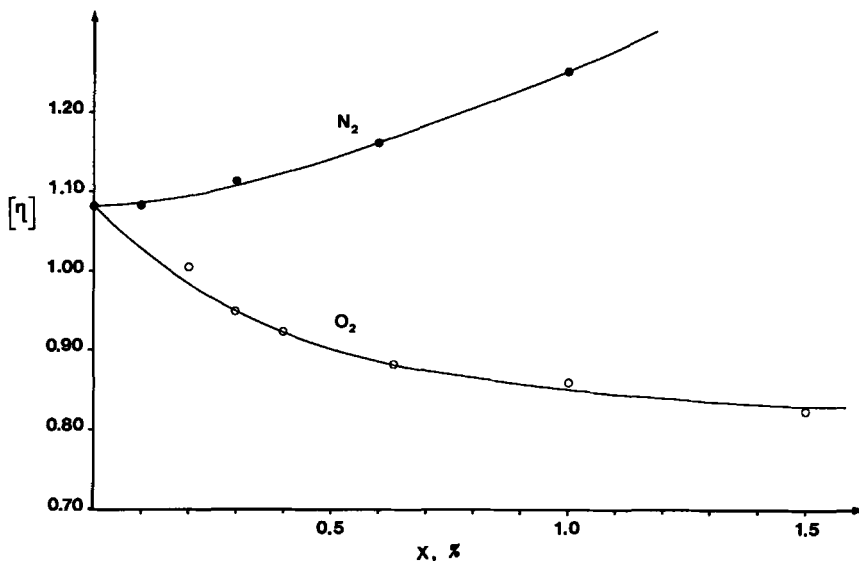
Fig. 10. Intrinsic viscosity as a function of conversion x. Data obtained for Pevikon R-45 at 190°C in oxygen (O) and nitrogen (●).

served already at the early stages of the degradation. At the same conversion, an increase in degradation temperature results in a less pronounced discoloration (Figs. 5 and 6) and an increased crosslinking (Tables III and IV). A cross dehydrochlorination mechanism as suggested by Druesedow and Gibbs[1] is in accordance with such a behavior:

$$\text{wCH=CH—CH=CH—CH—CH}_2\text{w} + \text{wCH}_2\text{—CH—CH}_2\text{—CH—CH—CH}w \rightarrow$$

with Cl substituents and an H, forming

$$\text{wCH=CH—CH=CH—CH—CH}_2\text{w}$$
$$\text{wCH}_2\text{—CH—CH}_2\text{—CH—CH—CH}w \quad + \text{ HCl} \quad (2)$$
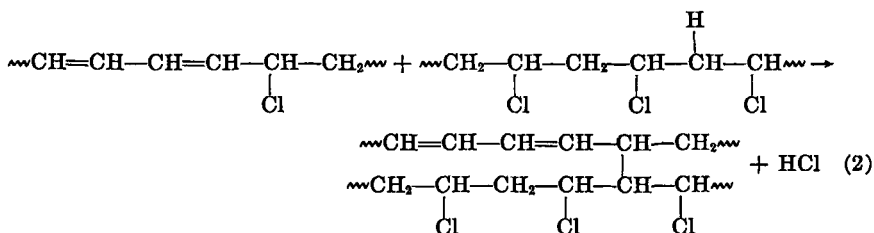
This type of elimination is similar to the intramolecular unimolecular mechanism proposed above, reaction (1). A prerequisite for this reaction is highly activated chlorine atoms, such as those β to random unsaturation. However, such structures initially show a higher tendency to form polyene sequences. The activation energy for the zipper reaction is believed to pass through a minimum with increasing length of the polyene sequence. The crosslinking reaction which will terminate the growing polyene chain is therefore gradually favored. An increase in degradation temperature was also found to increase the crosslinking (Tables III and IV). This may

be due to the higher activation energy for this reaction. At higher temperature, a larger number of initiation sites may be activated as well. At constant conversion, the latter effect will result in a shorter average polyene chain length. The connection between a higher crosslinking and a lower discoloration (Figs. 5 and 6) at higher temperatures is explained by the above-mentioned type of reasoning. The higher extent of crosslinking at constant conversion for Pevikon R-341 compared to Pevikon R-45 may as well be due to such reasons.

The dehydrochlorination in oxygen is much faster than in nitrogen. This supposedly is due to the superposition of oxygen-initiated radical
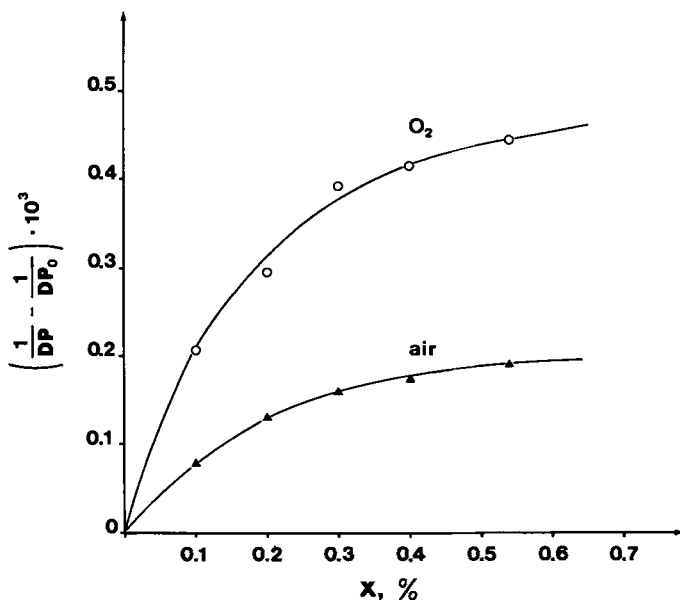
Fig. 11. Number of chain scissions per monomer unit as a function of conversion. Data for Pevikon R-45 at 190°C in air (▲) and oxygen (○).

processes on the dehydrochlorination reactions mentioned above.[32] Polyene sequences are thus initiated at a larger number of sites. This does not exclude the possibility that the propagation reaction is exclusively of the nonradical, unimolecular type. Our findings that the activation energies in oxygen and nitrogen are almost the same might indicate this.

Our results show that chain scission but no crosslinking occurs during the early stages of thermal degradation in oxygen ($x \leqslant 1.5\%$). At higher conversions, however, extensive crosslinking has been reported.[40,41] In accordance with our findings, chain scission mechanisms are assumed to include an oxygen attack. Reaction schemes similar to that proposed by Winkler[35] have often been suggested:[38,41−44]

$$R\cdot + \text{\textasciitilde}CH_2\text{---}CHCl\text{---}CH_2\text{---}CHCl\text{\textasciitilde} \rightarrow RH + \text{\textasciitilde}CH_2\text{---}CHCl\text{---}\dot{C}H\text{---}CHCl\text{\textasciitilde}$$

$$\text{\textasciitilde}CH_2\text{---}CHCl\text{---}\dot{C}H\text{---}CHCl\text{\textasciitilde} \xrightarrow{O_2} \text{\textasciitilde}CH_2\text{---}CHCl\text{---}\underset{\overset{|}{\underset{O}{O}}}{C}H\text{---}CHCl\text{\textasciitilde}$$

$$\text{\textasciitilde}CH_2\text{---}CHCl\text{---}\underset{\overset{|}{\underset{O}{O}}}{C}H\text{---}CHCl\text{\textasciitilde} + RH \rightarrow \text{\textasciitilde}CH_2\text{---}CHCl\text{---}\underset{\overset{|}{\underset{O}{O}}}{\overset{H}{\underset{|}{O}}}\text{---}CHCl\text{\textasciitilde} + R\cdot$$

(3)

$$CH_2\text{---}CHCl\text{---}\underset{\overset{O}{\underset{|}{O}}}{\overset{H}{\underset{|}{O}}}H\text{---}CHCl\text{\textasciitilde} \rightarrow \text{\textasciitilde}CH_2\text{---}CHCl\text{---}\underset{\overset{|}{\underset{O}{O}}}{C}H\text{---}CHCl\text{\textasciitilde} + OH\cdot$$

$$\text{\textasciitilde}CH_2\text{---}CHCl\text{---}\underset{\overset{|}{\underset{O}{O}}}{C}H\text{---}CHCl\text{\textasciitilde} \rightarrow \text{\textasciitilde}CH_2\text{---}CHCl\text{---}\underset{\overset{|}{\underset{O}{O}}}{C}H + \cdot CHCl\text{\textasciitilde}$$

This reaction scheme is based on work on olefinic model compounds.[45,46]

Stapfer and Granick[44] postulated a number of mechanisms for the degradation of PVC in oxygen. One of them implies an intermediate allylic carbanion:

$$\text{---}CH\text{=}CH\text{---}\underset{\overset{|}{Cl}}{C}H\text{---} \rightarrow \overset{\ominus}{\text{---}CH\text{\textbf{...}}CH\text{\textbf{...}}\underset{\overset{|}{Cl}}{C}(H)\text{---}} \xrightarrow{O_2} \text{---}CH\text{=}CH\text{---}\underset{\overset{|}{Cl}}{\overset{OOH}{\underset{|}{C}}}\text{---} \rightarrow$$

$$\text{---}CH\text{=}CH\text{---}\underset{\overset{|}{Cl}}{\overset{O}{\underset{|}{C}}}\text{---} + \cdot OH \quad (4)$$

The resulting alkoxy radical then supposedly lead to crosslinking or chain scission.

Our results can be well explained by β-scissions of alkoxy radicals.[35,38,42-44] It is reasonable to believe that the oxygen attack will preferably occur at allylically activated sites. Thus, the oxygen attack will terminate a growing polyene sequence:

$$\text{\textasciitilde}CH\text{=}CH\text{---}\underset{\overset{|}{Cl}}{\overset{H}{\underset{|}{C}}}\text{---}CH_2\text{\textasciitilde} \xrightarrow{O_2} \text{\textasciitilde}CH\text{=}CH\text{---}\underset{\overset{|}{Cl}}{\overset{OOH}{\underset{|}{C}}}\text{---}CH_2\text{\textasciitilde} \rightarrow$$

$$\text{\textasciitilde}CH\text{=}CH\text{---}\underset{\overset{|}{Cl}}{\overset{O}{\underset{|}{C}}}\text{---}CH_2\text{\textasciitilde} + HO\cdot \rightarrow \text{\textasciitilde}CH\text{=}CH\text{---}C\overset{\overset{O}{\diagup\diagup}}{\diagdown_{Cl}} + \cdot CH_2\text{\textasciitilde} \quad (5)$$

As can be seen from Figure 11, the extent of chain scission will soon become appreciably higher than expected from the number of internal double
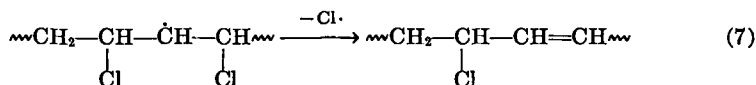
bonds. However, the radicals formed during chain scission will to some extent abstract hydrogen atoms from other polymer chains:

$$\underset{\underset{Cl}{|}}{\text{w}CH_2-CH}-CH_2-\underset{\underset{Cl}{|}}{CH}\text{w} \xrightarrow{\overset{\cdot OH}{\cdot CH_2\text{w}}} \text{w}CH_2-\underset{\underset{Cl}{|}}{CH}-\dot{C}H-CH\text{w} \qquad (6)$$
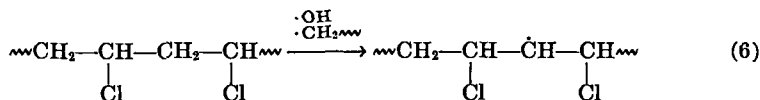
The new radicals might be directly attacked by oxygen according to reaction (3). Another possibility is the formation of new polyene chains:

$$\text{w}CH_2-\underset{\underset{Cl}{|}}{CH}-\dot{C}H-\underset{\underset{Cl}{|}}{CH}\text{w} \xrightarrow{-Cl\cdot} \text{w}CH_2-\underset{\underset{Cl}{|}}{CH}-CH{=}CH\text{w} \qquad (7)$$

The latter is supported by the fact that the dehydrochlorination is greatly enhanced in oxygen.

Compared to Pevikon R-341, Pevikon R-45 shows a higher rate of dehydrochlorination and a larger extent of chain scission during thermal degradation in oxygen (Fig. 7, Table III). This should be a plausible effect of the higher content of internal double bonds in Pevikon R-45.

References

1. D. Druesedow and C. G. Gibbs, *Nat. Bur. Stand. Circular No. 525*, 69(1953).
2. E. J. Arlman, *J. Polym. Sci.*, **12**, 543 (1954).
3. B. Baum and L. H. Wartman, *J. Polym. Sci.*, **28**, 537 (1958).
4. D. K. Taylor, *Plast. Inst. Trans.*, **28**, 170 (1960).
5. G. Talamini and G. Pezzin, *Makromol. Chem.*, **39**, 26 (1960).
6. B. Dolezel and J. Stepek, *Chem. Prum.*, **10**, 381 (1960).
7. M. Lizy and S. Varda, *Chem. Zvesti*, **14**, 14 (1960).
8. B. Baum, *SPE J.*, **17**, 71 (1961).
9. M. Lizy, *Chem. Zvesti*, **19**, 84 (1965).
10. W. C. Geddes, *Eur. Polym. J.*, **3**, 267 (1967).
11. D. Braun and R. F. Bender, *Eur. Polym. J., Suppl.*, 269 (1969).
12. C. F. Bersch, M. R. Harvey, and B. G. Achhammer, *J. Res. Nat. Bur. Stand.*, **60**, 481 (1958).
13. A. Komsha, *Nippon Kagaku Zasshi*, **78**, 1517 (1958).
14. A. A. Berlin, *Dokl. Akad. Nauk SSSR*, **144**, 1042 (1962).
15. K. S. Minsker, E. O. Krats, and I. Pakhomova, *Vysokomol. Soedin.*, **A12** (3), 483 (1970).
16. E. J. Arlman, *J. Polym. Sci.*, **12**, 547 (1954).
17. A. A. Berlin and V. F. Prosvirkina, *Soviet Plast.*, **5**, 8 (1965).
18. A. Rieche, A. Grimm, and H. Mücke, *Kunststoffe*, **52**, 265 (1962).
19. W. I. Bengough and H. M. Sharpe, *Makromol. Chem.*, **66**, 31 (1963).
20. S. Siggia, *Quantitative Organic Analyses via Functional Groups*, 3rd ed., Wiley, New York, 1963, p. 258.
21. K. B. Abbås and E. M. Sörvik, *J. Appl. Polym. Sci.*, **17**, 3567 (1973).
22. K. B. Andersson, *Determination of the Intrinsic Viscosity of PVC Solutions*, Accepted Nordforsk Standard, Stockholm, 1973.
23. M. R. Cannon, R. E. Manning, and J. D. Bell, *Anal. Chem.*, **32**, 255 (1960).

24. Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci.*, **B5**, 753 (1967).

25. M. Bohdanecký, K. Šolc, P. Kratochvíl, M. Kolinský, M. Ryska, and D. Lím, *J. Polym. Sci. A-2*, **5**, 343 (1967).

26. E. E. Drott and R. A. Mendelson, *Seminar Proceedings, 6th International Seminar on Gel Permeation Chromatography*, Miami Beach, October 1968.

27. Y. Shindo, M. Murakami, and T. Nishida, *J. Polym. Sci. B*, **10**, 555 (1972).

28. P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

29. W. C. Geddes, *Eur. Polym. J.*, **3**, 733 (1967).

30. P. Carstensen, paper presented at Nordiska Polymerdagarna, Göteborg, November 1969.

31. W. C. Geddes, *Rubber Chem. Technol.*, **40**, 177 (1967).

32. D. Braun, *Pure Appl. Chem.*, **26**, 173 (1971).

33. M. Asahina and M. Onozuka, *J. Polym. Sci.*, **A-2**, 3505, 3515 (1964).

34. T. Suzuki and N. Nakamura, *Jap. Plast.*, **4**, 16 (1970).

35. D. E. Winkler, *J. Polym. Sci.*, **35**, 3 (1959).

36. R. R. Stromberg, S. Straus, and B. G. Achhammer, *J. Polym. Sci.*, **35**, 355 (1959).

37. A. Guyot and J. P. Benevise, *J. Appl. Polym. Sci.*, **6**, 103 (1962).

38. J. E. Campbell and W. M. Rauscher, *J. Polym. Sci.*, **18**, 461 (1955).

39. M. Imoto and T. Nakaya, *Kogyo Kagajaku Zasshi*, **68**, 2283 (1965).

40. M. Imoto and T. Otsu, *J. Inst. Polytech., Osaka City Univ., Ser. C*, **4**, 1 (1953).

41. W. I. Bengough and H. M. Sharpe, *Makromol. Chem.*, **66**, 45 (1963).

42. W. Jashing, *Kunststoffe*, **52**, 458 (1962).

43. W. Reichert, *Plast. Kaut.*, **14**(2), 79 (1967).

44. C. H. Stapfer and J. D. Granick, *Proc. 167 Meeting, ACS Organic Coatings and Plastics Chemistry*, **31**(1), 204 (1971).

45. N. Grassie, *Chemistry of High Polymer Degradation Processes*, Interscience, New York, 1956.

46. E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, and Vaughan, *Discuss. Faraday. Soc.*, **10**, 242 (1951).