On the Thermal Degradation of Poly(vinyl Chloride). III. Structural Changes During Degradation in Nitrogen

K. B. ABBÅS* and E. M. SÖRVIK, *The Polymer Group, Department of Organic Chemistry, Chalmers University of Technology and University of Gothenburg Fack, S-402 20 Göteborg 5, Sweden*

Synopsis

The structural changes in poly(vinyl chloride) during thermal degradation in nitrogen at 190°C have been investigated. From gel permeation chromatography analyses no chain scission, but only crosslinking reactions were observed. An increase in the molecular weight was measured even at 0.3% conversion. For longer polyene sequences and at higher conversions, a crosslinking reaction competed with the "zipper" propagation. The secondary reactions were more extensive at longer polyene sequence lengths. The growing polyene sequences can be terminated not only by branching reactions but also at existing pendent chloromethylene groups. A decrease in the amount of short chain branching with conversion also indicated other types of secondary reactions. Such a decrease was also observed during thermomechanical degradation in a Brabender Plastograph. The average polyene sequence length was calculated to be around 10, depending somewhat on the type of analysis used. Although allylic chlorine atoms seem to be the main points of initiation, other sites cannot be excluded as the number of initiation points increases appreciably during the early stages of the degradation. Such an increase is, of course, also consistent with a radical mechanism.

INTRODUCTION

Although the thermal degradation of poly(vinyl chloride) (PVC) has been extensively studied, many unsolved problems still remain. Kinetic studies of the dehydrohalogenation are rather common, but such studies combined with structural analysis of the degraded polymer are scarce.

Discoloration of PVC during degradation indicates that structural changes are occurring. These structural changes are well known, and the discoloration is explained by the development of conjugated double bonds (polyene sequences) formed through a "zipper" mechanism.[1] A sequence of about five conjugated double bonds is required to obtain discolored material.[2] The development of polyene sequences is usually analyzed by ultraviolet-visible spectroscopy, which gives information about sequence lengths between 3 and 14.[3–7] Methods for the calculation of the polyene sequence length distribution have been suggested.[4–6]

Molecular weight changes during degradation have normally been analyzed by intrinsic viscosity measurements, but these measurements do not provide

---

* Present address: Telefonaktiebolaget LM Ericsson 12625 Stockholm, Sweden.

any detailed information on structural changes like chain scission, or on molecular-enlargement reactions such as branching and crosslinking.[1,8] The amount of extensive branching leading to three-dimensional crosslinked structures has often been estimated from per cent insolubility and related parameters.[9–12] By the introduction of gel permeation chromatography (GPC), it has become easier to study not only molecular weight changes but also changes in molecular weight distribution (MWD).[13] In combination with intrinsic viscosity data, GPC is also a powerful tool for measurement of long chain branching (LCB). In our previous investigations the changes of MWD were studied both for thermo-oxidative and thermomechanical degradation of PVC.[14–16] It is the object of this study to analyze the structural changes during the thermal degradation of PVC in nitrogen and to relate these changes to the degree of dehydrochlorination. As a comparison, some results from thermomechanical degradation of PVC are also included.

EXPERIMENTAL

Materials

Two suspension-polymerized PVC resins (Pevikon R-45 and Pevikon R-150) and one emulsion-polymerized PVC resin (Pevikon K-25) were used. All samples were generously supplied by KemaNord AB, Sweden. Polymer data are given in Table I.

TABLE I
Data of Investigated Resins

Polymer	$\overline{M}_n$	$\overline{M}_w$	H	CH$_3$ per 1000 C[a]
Pevikon R-45	49,000	118,000	2.4	5.1
Pevikon R-150	25,800	54,000	2.1	6.1
Pevikon K-25	53,000	122,000	2.3	4.9

[a] Measured on reduced samples.

Tetrahydrofuran (THF) was refluxed over sodium borohydride until no peroxides could be detected.[17] It was then distilled under nitrogen from metallic sodium. Methanol and acetone were puriss grade. All other reagents and solvents were analytical grade.

Nitrogen containing less than 10 ppm oxygen was used. The gas was supplied and analyzed by AGA, Sweden.

Dehydrochlorination Kinetics

Pevikon R-45 was heated in streaming nitrogen to different degrees of dehydrochlorination. Evolved hydrogen chloride was detected by conductometry. The sample size was 1 g. Unless otherwise stated, the experiments were carried out at 190°C and to a maximum of 1.5% conversion. The degree of dehydrochlorination or the conversion, x%, is determined as the ratio between the hydrogen chloride evolved and the total available amount. A de-

tailed description of the dehydrochlorination apparatus has been given earlier.[18]

Brabender Plastograph

Samples of Pevikon R-150 and Pevikon K-25 were treated for different lengths of time in a Brabender Plastograph at a block temperature of 160 ± 3°C. The experimental details have been given in a previous paper.[14]

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 from 4 to 6 hr before analysis. To avoid oxidation of the polyene sequences, the solutions also have to be free from peroxides.[4,19] In order to obtain peroxide-free solutions, the THF was treated as above (see "Materials").

Viscometry

Intrinsic viscosities were measured at 25°C with the use of Cannon-Ubbelohde viscometers adapted for dilution. Kinetic energy corrections[20] 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 were then heated in autoclaves for 3 hr at 120°C to get rid of molecular aggregates.[14,15] After cooling, they were filtered under pressure through a Kreuger asbestos filter (1 μ). The intrinsic viscosities were obtained in the concentration range: 2–5 g/l. Each sample was measured at least twice.

Gel Permeation Chromatography

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., Milford, Mass.).

The concept of universal calibration proposed by Benoit et al.[21] 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 calibration, we used a relationship proposed by Bohdanecký et al.[22]:

$$[\eta] = 1.5 \cdot 10^{-4} \cdot \bar{M}_w^{0.77} \text{ dl/g.}$$

This equation corrects the intrinsic viscosity values for polydispersity.

The polyene sequences appearing in degraded PVC will cause stiffer polymer chains. This has been found to decrease the intrinsic viscosity and thus

affect the determination of molecular weights.[23]   At low degrees of dehydro-
chlorination (1–2%), this effect is within experimental error.

Molecular weights and molecular weight distributions were calculated by a
computer program devised by Drott and Mendelson.[24]   The ratio of the in-
trinsic viscosity of a branched molecule to that of a linear molecule having the
same molecular weight has been related to the number of branch points
through the function g as follows:

$$[\eta]_{br}/[\eta]_l = g^b,$$

where b depends on the branching model that is used.   According to Zimm
and Kilb[25] a value of $b = 0.5$ is in better agreement with experimental data
than $b = 1.5$, which has been suggested earlier.[26]   The former value was
therefore used in this investigation.   For polydisperse samples, the g-value is
related to the weight number of trifunctional branch points per molecule in
the following way[25]:

$$\langle g_3 \rangle_w = \frac{6}{n_w} \left[0.5 \left(\frac{2 + n_w}{n_w} \right)^{0.5} \ln \frac{(2 + n_w)^{0.5} + n_w^{0.5}}{(2 + n_w)^{0.5} - n_w^{0.5}} - 1 \right]$$

The corresponding relationship for tetrafunctional branches is expressed as:

$$\langle g_4 \rangle_w = 1/n_w \cdot \ln (1 + n_w)$$

The above mentioned computer program was used to calculate the trifunc-
tional LCB and the corrected MWD.   The tetrafunctional LCB was obtained
from g-values.

Ozonation

The sample was swelled in chloroform; a small amount of methanol was
added; and ozonation was carried out for 3 hr at room temperature according
to a procedure described elsewhere.[16]   Contrary to the results obtained by
Michel et al.,[27] no side reactions were observed at this temperature.   No fur-
ther decrease in the molecular weight was found after 2 hr.

Methyl Content

The methyl content was determined according to Method B in the ASTM
standard.[28]   A double-beam Beckman IR-9 Spectrophotometer was used.
The IUPAC high density polyethylene (narrow molecular weight distribu-
tion); was utilized as wedge material.[29]   The methyl content was obtained
from:

$$CH_3/1000 \, C = K \cdot \frac{A_{1378}}{d \cdot t}$$

where

A_{1378} = absorbance of the sample at 1378 cm^{-1}
    d = sample density
    t = sample thickness

The calibration was carried out on IUPAC low density polyethylene (LDPE
B) with a methyl content of 28.3 CH$_3$/1000 C[29].   This resulted in a K-value of

9.9. The films of reduced PVC were prepared as described below. The thickness of each film was measured with a Frank Prufgeräte Measuring Device. The accuracy of the measurement of the film thickness was estimated to ±0.0005 cm. The density of every sample was measured with high accuracy (±0.002 g/cm^3) in a density gradient column at 23°C. Most densities were around 0.950 g/cm^3. The methyl content was determined with an overall accuracy of about ±5%.

PVC Reduction

The procedure used is similar to that reported by Carrega et al.[30] The hydrogenation reaction took place in 135-ml stainless steel autoclaves. The autoclaves, each charged with 2.5 g of reprecipitated PVC, were put into a glovebox together with all reagents needed. The glovebox was then purged with extra-pure nitrogen (<30 ppm O_2) for about 20 hr to obtain an inert atmosphere. After that a solution of $LiAlH_4$ in THF (ca. 1 mole/l.) was prepared, and 50 ml of this solution were poured into each autoclave. The autoclaves were then carefully tightened and rotated in a thermostat for seven days at 100°C. The hydrogenated PVC was first separated from residual reaction reagents by pouring it into ice-cooled 6N hydrochloric acid. As much as possible of the liquid phase was then siphoned off, and 120 ml of Decalin and 80 ml of concentrated hydrochloric acid were added. This mixture was heated under nitrogen until the polymer was completely dissolved in the Decalin phase. The mixture was then refluxed for about half an hour and was poured into a separation funnel, which was heated to prevent the polymer from precipitating. The inorganic phase was separated from the polymer phase, and an additional 80 ml of concentrated hydrochloric acid were added; and the above procedure was repeated. The Decalin phase was then precipitated into ice-cooled acetone. The polymer was thoroughly washed with acetone and was kept at 50°C for 2–3 days.

Film Preparation

The samples obtained from the hydrogenation reaction were pressed under a Carver laboratory press. A 0.02-cm-thick plate with a cylindrical hole was used as a spacer. The press temperature was 140° to 150°C. The polymer was preheated for 5 min before a continuously increasing pressure was applied. The pressure was released at 3000 kP, and the film formed was then removed from the press and cooled.

RESULTS AND DISCUSSION

Molecular Weight Distribution

The dehydrochlorination apparatus used was designed to give a quick response.[15,18] Temperature equilibrium was reached after less than 5 min. After this period the rate of dehydrochlorination was constant. A significant discoloration was observed at 0.1% conversion. No insoluble material was obtained up to 1.0% dehydrochlorination. At 1.5%, however, about 6% insol-
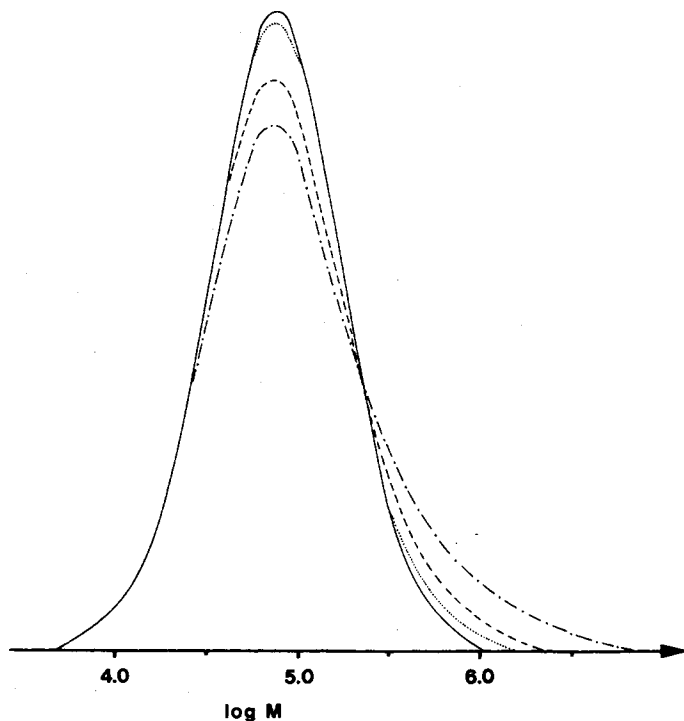
Fig. 1. Molecular weight distributions for Pevikon R-45 degraded in nitrogen at 190°C: (———) = original polymer; (·····) = at 0.3% conversion; (– – – –) = at 0.54% conversion; and (–·–·–) = at 1.0% conversion.

uble material remained after the sample was heated in THF for 3 hr at 120°C. The molecular weight distributions of the original and degraded samples are shown in Figure 1, and the molecular weight averages in Table II. As can be seen, a distinct increase in the high molecular weight end was first observed at 0.30% conversion. The effect became more pronounced the higher the degree of dehydrochlorination. In agreement with earlier findings,[15,16] no chain scission, but only molecular enlargement, was observed. The formation of high molecular weight material has been found to be the result of

TABLE II
Changes in Molecular Weight Averages and Methyl Content
with Degree of Dehydrochlorination: Thermal Degradation
of Pevikon R-45 in Nitrogen at 190°C

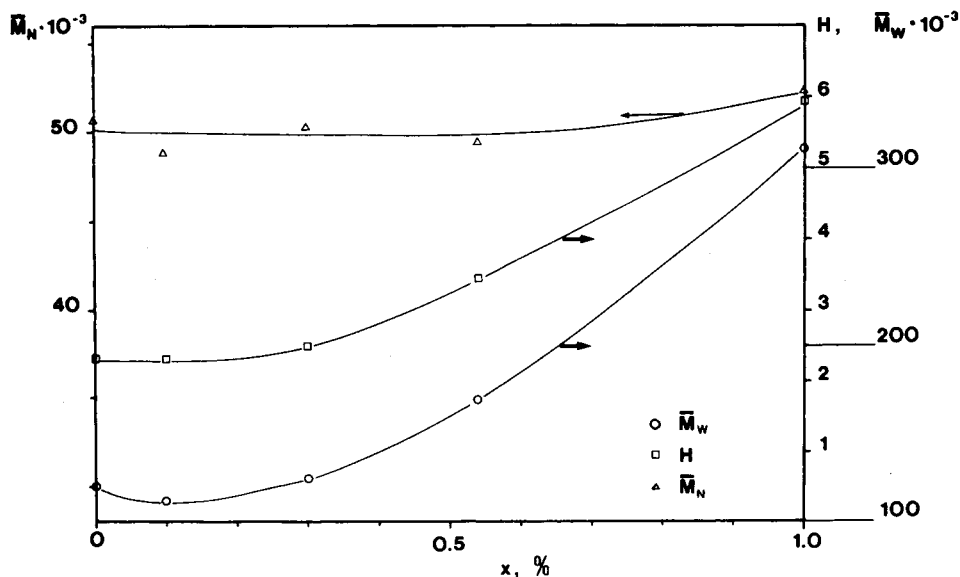| Conversion, x, %	Time of degradation, min	$\overline{M}_n$	$\overline{M}_w$	H	$CH_3/1000$ C
0.00	0	49,000	118,000	2.4	—
0.10	—	48,800	112,000	2.3	5.1
0.20	13.2	—	—	—	—
0.30	17.7	50,300	125,000	2.5	5.1
0.40	21.6	—	—	—	—
0.54	28.4	49,500	169,900	3.4	4.6
0.80	38.4	—	—	—	—
1.00	51.0	52,400	311,000	5.9	4.2

Fig. 2. Heterogeneity index *(H)*, weight-average molecular weight $(\bar{M}_w)$, and number-average molecular weight $(\bar{M}_n)$ as a function of conversion. Pevikon R-45 degraded in nitrogen at 190°C.

crosslinking reactions.[1,3,5,8,15,16] However, the exact nature of these reactions is not yet known.

Heterogeneity index, H, $(\bar{M}_w/\bar{M}_n)$, $\bar{M}_n$, and $\bar{M}_w$, respectively, are plotted versus x in Figure 2. The high increase in $\bar{M}_w$ clearly reflects the larger amount of high molecular weight material formed (see Table II). As $\bar{M}_n$ is nearly constant, the heterogeneity index shows almost the same relative changes as $\bar{M}_w$. From Figure 1 and Figure 2 it is evident that branching reactions start at very low degrees of dehydrochlorination. They are detectable by GPC at 0.30% conversion, but may begin even earlier.

TABLE III
Changes in Molecular Weight Averages and Methyl Content
as a Function of Degradation Time: Thermomechanical Degradation
of Pevikon R-150 and Pevikon K-25 in a Brabender Plastograph

Polymer	Time of degrada- tion, min	Mass tem- perature, °C[a]	$\bar{M}_n$	$\bar{M}_w$	CH₃ per 1000 C
Pevikon R-150	0	—	29,400[b]	59,800[b]	6.1
Pevikon R-150	2	170	30,600	62,600	6.0
Pevikon R-150	4	172	30,600	62,900	6.1
Pevikon R-150	6	174	29,800	60,200	6.4
Pevikon R-150	8	174	29,800	62,200	5.8
Pevikon R-150	10	174	30,400	62,800	5.3
Pevikon K-25	0	—	53,000	122,000	4.9
Pevikon K-25	1	172	50,300	120,500	4.9
Pevikon K-25	4	194	50,400	177,300	4.3

[a] The wall temperature of the kneading chamber was $160 \pm 3°C$.
[b] The molecular weights of the virgin Pevikon R-150 reported here are somewhat higher than those given in Table I. The use of different GPC calibrations is the explanation for these discrepancies.
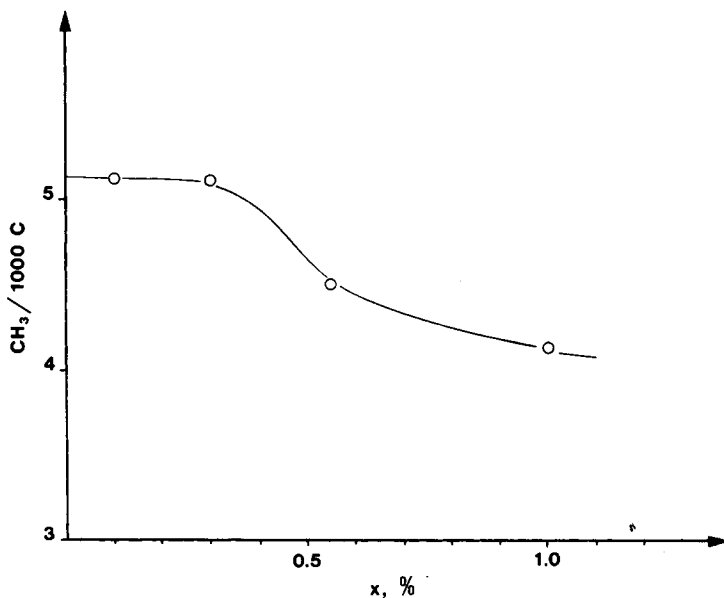
Fig. 3. Methyl content in reduced PVC as a function of conversion. Pevikon R-45 degraded in nitrogen at 190°C.
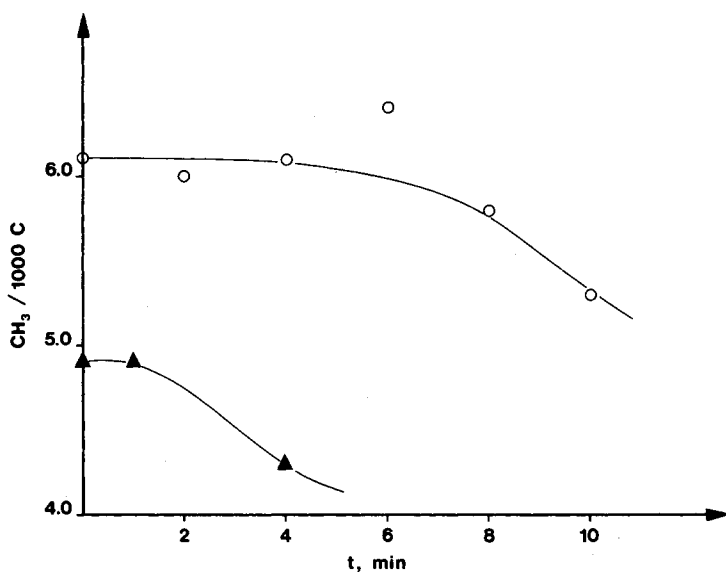
Fig. 4. Methyl content in reduced PVC as a function of degradation time; degradation in a Brabender Plastograph with a heating temperature of 160°C: (O) = Pevikon R-150; (▲) = Pevikon K-25.

Methyl Content

In Table II and Figure 3 the changes in methyl content in the reduced PVC are shown. At first no change was observed, but at conversions higher than 0.30% the samples showed a decrease in methyl content. This decrease was detected at nearly the same conversion as the increase in the weight-average

molecular weight. The number of methyl groups per 1000 C decreased by one during the loss of 1% of the total HCl content.

A similar drop in the methyl content was observed during thermomechanical degradation in a Brabender Plastograph.[14] The results for Pevikon R-150 and Pevikon K-25 are shown in Table III and Figure 4. Pevikon K-25 showed a decrease in methyl content much earlier than Pevikon R-150, but also reached higher mass temperatures earlier. The temperature and molecular weight at different degradation times are given in Table III. The Brabender Plastograph had a block temperature of $160 \pm 3°C$. At the time when the decrease in methyl content was observed, the polymers were highly discolored. Further degradation resulted in the formation of insoluble material.

Branching

The amount of branching in Pevikon R-45 at different degrees of dehydrochlorination is shown in Table IV and Figure 5. After 0.30% conversion, the amount of LCB increased almost linearly. A simultaneous decrease in short chain branching (SCB) was also observed. It has been suggested that the long branches are formed through intermolecular condensation.[8] At higher

TABLE IV
Branching at Different Degrees of Dehydrochlorination:
Thermal Degradation of Pevikon R-45 in Nitrogen at 190°C

Degree of Dehydro- chlorination, %	$\overline{M}_w$	Trifunctional branch points per molecule	Tetra- functional branch points per molecule	Tetra- functional LCB per 1000 C	SCB per 1000 C
0.00	118,000	0.71	0.28	0.07	4.4
0.10	112,600	0.56	0.23	0.06	4.3
0.30	125,700	0.63	0.25	0.06	4.4
0.54	171,600	2.06	0.80	0.15	3.7
1.00	312,900	7.51	2.84	0.28	3.3

degrees of dehydrochlorination, Diels-Alder reactions may also occur. Both types of reactions form tetrafunctional branches; but if one of the reacting centers is located close to a chain end, the long branches formed can be considered trifunctional. If both reacting centers are close to chain ends, only short branches will occur. Although the majority of crosslinking reactions result in tetrafunctional LCB, the amount of trifunctional LCB was calculated as a comparison.

The amount of SCB was calculated by subtracting LCB and one methyl group per molecule from the total methyl content. This procedure assumes that only half of the chain ends in the reduced polymer have methyl groups. Baum and Wartman[31] found from ozonolysis experiments that 60% of the molecules have double bonds at the end of the chain. In a more recent investigation Carrega et al.[30] determined the difference in methyl content after hydrogenation by $LiAlH_4$ and a following reduction by Raney Nickel. The latter reagent was supposed to reduce even the chloro-containing double bonds

Fig. 5. SCB and LCB as a function of conversion. Pevikon R-45 degraded in nitrogen at 190°C.

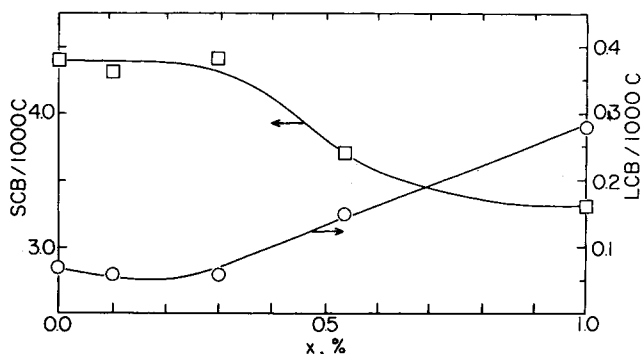at chain ends. Carrega and co-workers thus found that every molecule contains one 1-chlorovinyl (—CH=CHCl) end group. If this is the case, the other end groups are saturated groups or initiator fragments. The latter are very few: approximately every fourth molecule has been found to contain an initiator residue.[32] From this it is obvious that subtracting one methyl group per molecule from the total amount will give a reasonably good estimate of the total degree of branching.

There are different reasons for the decrease in the amount of SCB. The development of unreducible end groups during the degradation is a possible artifact. Thus, a (—CH—CH$_3$) group can be converted to (—CH=CH$_2$),

        Cl

which is unaffected by the LiAlH$_4$ treatment.[30] Such reactions are, of course, more probable, the higher the conversion is. Cyclization reactions at branch points and/or chain ends will also result in a lower number of small chain branches.

Polyene Sequences

The formation of polyene sequences during thermal degradation of PVC has often been followed by ultraviolet-visible spectroscopy. Figure 6 shows the changes in transmission at different conversions. The transmission decreases with higher conversion in a manner generally observed. As mentioned above, the sample, at 1.50%, was not completely soluble. Through studies of model compounds for polyenes of different lengths, it has been found that the highest peak in the absorption spectrum for each compound occurs at the highest wavelength when $n \geq 5$.[33-36] In these works it was also concluded that the relationship between the wavelength of the absorption peak, λ, and the polyene sequence length, n, could be expressed by the equation

$$\lambda = k \cdot \sqrt{n} + k',$$

where k and k' are constants.[35] This relationship was found to hold for dimethyl polyenes of lengths between 3 and 12, but has sometimes been used even for somewhat longer sequences. In three papers, Braun et al.[4,5,37] stud-
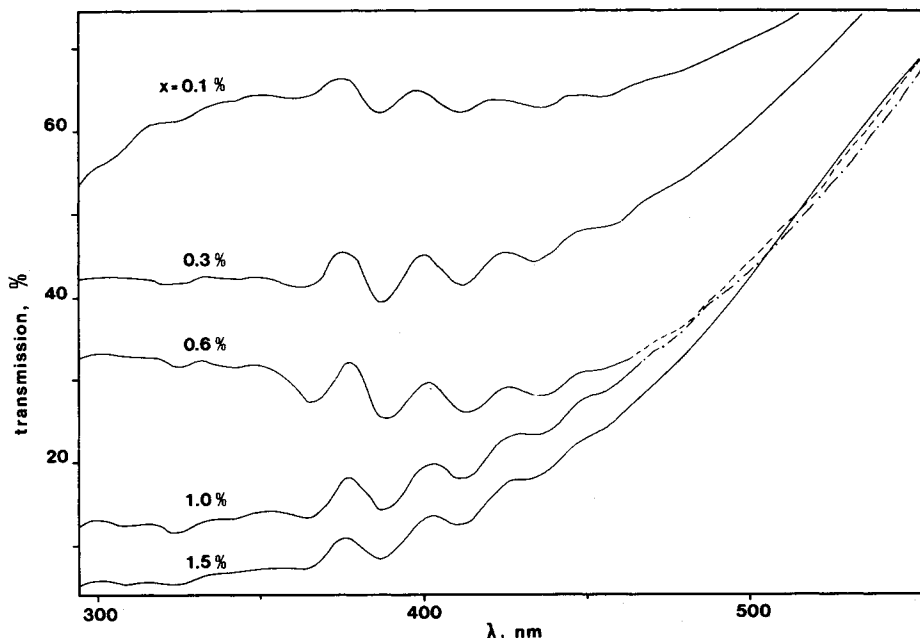
Fig. 6. Ultraviolet-visible spectra of Pevikon R-45 at different conversions.

ied the changes in distribution of polyene sequences during thermal degradation of halogenated polymers, mainly of PVC. The analyses showed that every maximum in the absorption spectra could, to a good approximation, be related to a certain sequence length. Especially at higher lengths ($n \geq 8$) the data for PVC obeyed the equation $\lambda = k \cdot \sqrt{n} + k'$ very well. Braun et al.[4,5] also derived different measures of the polyene distributions and followed their changes as a function of degradation.

There have been some speculations why the polyene sequences have limited lengths: Braun suggested that after a certain length of the polyene sequence, it will reach a state when an additional HCl split-off will not be as energetically favorable as in the beginning and other reactions may therefore compete.[7] Another explanation was recently put forward by Guyot et al.[38] Studying the reactions of model substances, they concluded that readdition of HCl occurred during degradation and that the limited polyene sequence length may be the result of this equilibrium. In addition, secondary reactions, especially intermolecular condensation and in some cases Diels-Alder reactions, can disrupt the growing polyene sequences.[4,8,15] From our earlier investigations the intermolecular condensation reactions seem to be of great importance, and our new measurements also stress this fact.

From data in Table V (Fig. 6) the absorption at different maxima has been plotted versus conversion in a log–log graph shown in Figure 7. The curves representing the different polyene sequences have been shifted in order to get a clearer picture. All curves are linear at the early stages, but deviate from linearity at higher conversions (x limit). The deviations have been drawn as straight lines although they are probably continuously deviating. The straight lines are expressed by equations like

TABLE V
Variation of Optical Absorbance with Polyene Sequence Length and Conversion:
Degradation of Pevikon R-45 in Nitrogen at 190°C

Polyene sequence length	Wavelength, λ(mμ)	Optical absorbance at different conversions					
		0.20%	0.30%	0.40%	0.54%	0.80%	1.00%
3	288	0.238	0.298	0.387	0.509	0.724	0.839
4	308	0.223	0.285	0.378	0.484	0.699	0.788
5	324	0.228	0.299	0.393	0.503	0.723	0.801
6	340	0.223	0.300	0.395	0.501	0.699	0.772
7	364	0.246	0.337	0.443	0.561	0.738	0.812
8	388	0.267	0.370	0.483	0.602	0.760	0.824
9	412	0.267	0.375	0.484	0.590	0.706	0.760
10	435	0.259	0.362	0.467	0.554	0.642	0.878
11	455	0.244	0.337	0.431	0.509	0.572	0.599
12	475	0.221	0.303	0.388	0.455	0.499	0.519

$$A = C \cdot x^{\alpha},$$

where A is the absorption for a certain polyene, x is the conversion, and C and α are constants. The deviation from linearity indicates that the kinetic chain for the polyene growth was interrupted. The deviation appears earlier and it was also more pronounced for the longer polyene sequences. The conversion at which the deviation occurs is rather well defined for all polyene sequence lengths. However, the extent of deviation can be determined with high accuracy for longer polyene sequences only ($n \geq 8$). At sufficiently long times of degradation even short polyene sequences may undergo secondary reactions, although these reactions were favored by longer polyenes.[39] As branching reactions were observed simultaneously, this indicated that the secondary reactions were mainly of this type.[15,16] The conversion at deviation from linearity, x limit, is plotted versus the polyene sequence length in Figure 8. As can be seen from Figure 8, the curve for $n = 9$ deviates at a conversion about 0.3% lower than in the case when $n = 5$. Or, expressed in another way: the secondary reactions occurred more easily when n exceeded 5.
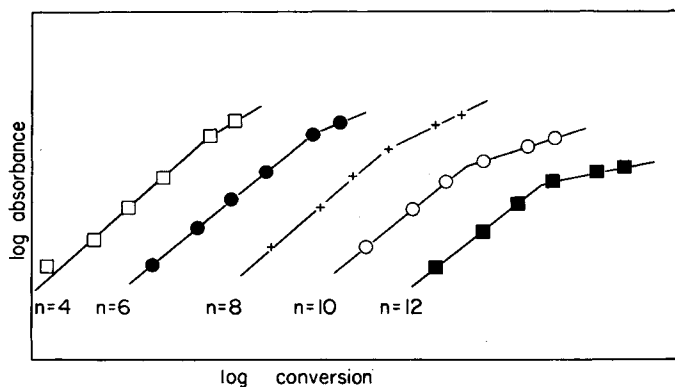

Fig. 7. A log–log plot of absorbance vs. conversion for even numbers of polyene sequence lengths. Pevikon R-45 degraded in nitrogen at 190°C.
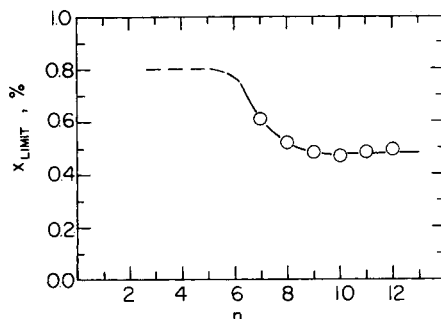
Fig. 8. The conversion at deviation from linearity in Fig. 7, x limit, as a function of polyene sequence length. Pevikon R-45 degraded in nitrogen at 190°C.

From Figure 8 it is evident that a competition between a sequence growth and a secondary reaction is especially noticeable for polyene sequences exceeding about 7 units in length. The rates for the formation of different polyene sequences showed a flat maximum between $n = 6$ and $n = 9$. From these experiments it seems likely that the most probable polyene sequence length is somewhat below 10 units, which is also in very good agreement with earlier data.[1,3,4,7,40] The secondary reactions were thus favored by long polyene sequences and high conversions. For $n = 12$, these reactions were first detectable at about 0.5% conversion. At this time a measurable increase in LCB and $\bar{M}_w$ was also observed. From kinetic considerations, the formation and distribution of polyene sequences in degraded PVC have been calculated.[41] From this investigation an average polyene sequence length of about 7 was determined for the actual polymer. In addition, a value around $n = 10$ was also found from ozonolysis data (see below).
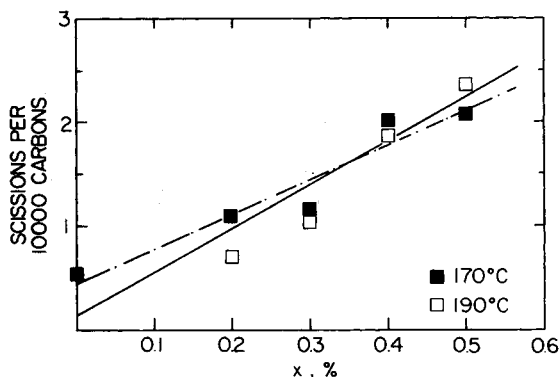
Fig. 9. Number of scissions during ozonolysis as a function of conversion. Pevikon R-45 degraded in nitrogen.

The importance of crosslinking reactions as chain-stoppers for the growing polyene sequences was estimated from LCB data given in Table IV. For tetrafunctional units, a value of 18 double bonds per branch was obtained at 0.54% conversion. The corresponding figure for trifunctional units was 7 double bonds per branch; but as mentioned above, such branches are less probable. Almost exactly the same values were calculated at 1.00%. As the

accuracy is lower at lower conversions, the data below 0.54% was not treated. The branching of the original polymer was considered negligible. Assuming an average polyene sequence length of about 10, the data led to the conclusion that more than 50% of the polyenes were terminated by intermolecular reactions.

Certain of the existing irregularities in the ideal PVC structure have also been considered as termination sites for growing polyene sequences. As the number of such structures is very low, the contribution to termination reactions is negligible.[7] Short chain branches have so far not been considered as termination points. Recently, however, it has been found by C^{13}—NMR investigations that the short branches in PVC are mainly chloromethyl groups and not C_4—chains as suggested earlier.[42] A mechanism for the formation of such pendent groups has been given by Talamini and co-workers.[43] Unlike the longer side chains, the chloromethyl structures can act as termination points for a propagating polyene:

$$\text{---CH---CH}\!=\!\text{CH---CH---CH---CH}_2\text{---CH---} \longrightarrow$$

with substituents Cl, CH_2Cl, Cl

$$\text{---CH---CH}\!=\!\text{CH---CH}\!=\!\text{C---CH}_2\text{---CH---} + \text{HCl}$$

with substituents CH_2Cl, Cl

or if the polyene is growing from the other side:

$$\text{---CH}_2\text{---CH---CH---CH}_2\text{---CH---CH}\!=\!\text{CH---} \longrightarrow$$

with substituents Cl, CH_2Cl, Cl

$$\text{---CH}_2\text{---CH---CH---CH}\!=\!\text{CH---CH}\!=\!\text{CH---} + \text{HCl}$$

with substituents Cl, CH_2Cl

Assuming $\bar{n} = 10$, the level of SCB given in Table IV will thus cause a probability of termination of about 20%. According to these data the SCB and the formation of LCB could terminate more than two thirds of all polyene sequences. Note, however, that the growing polyene sequences stop growing when the degradation experiment is interrupted.

An ozonolysis technique combined with GPC was used for the estimation of the average polyene sequence length.[16] This method was also used to find out if new initiation sites were formed during the degradation. The number-average molecular weight was measured at different degrees of dehydrochlorination before and after ozonolysis. The amount of scission caused by the breaking of double bonds was then determined. The result is illustrated by Figure 9.

If the degradation was initiated only at chain ends, the drop in $\bar{M}_n$ after ozonolysis should be very small. But as this drop was found to be considerable, initiation within the chains seems to be more important. The extent of chain-end initiation cannot be calculated from these data; however, from the agreement with peroxide contents, Geddes[40] considered it to be small. If degradation was initiated at the internal unsaturated groups only, the number of scissions for degraded samples ought to be almost the same as for the original polymer. The steep increase in the number of scission points at higher degrees of dehydrochlorination indicated that new initiation sites or

double bonds were formed within the chains during degradation. Geddes has used a similar technique and found the same type of changes.[40] However, our results were calculated at lower conversions in order to avoid the effect of crosslinking, which may begin to interact at rather low conversions.

If the initiation of polyene sequences at chain ends is negligible, the average polyene sequence length, $\bar{n}$, is obtained as follows:

$$\bar{n} = \frac{1}{(1/\overline{DP}_n - 1/\overline{DP}_n{}^\circ)} \cdot \frac{x}{100},$$

where $\overline{DP}_n$ is the number-average degree of polymerization of the ozonized polymer, $\overline{DP}_n{}^\circ$ is the number-average degree of polymerization of the unozonized polymer, and x is the degree of dehydrochlorination in per cent.

Geddes[40] found an average polyene sequence length of about 14. His degradation experiments were conducted in nitrogen at 150°C. By using the data in Figure 9, we found a corresponding value of about 14 at 170°C and about 11 at 190°C. These results are somewhat higher than those obtained from measurements by ultraviolet-visible spectroscopy. It should be kept in mind, however, that the average sequence length obtained by the ozonolysis technique can be somewhat overestimated, as scissions of polyenes close to, or at, chain ends affect the measurements very little.

Figure 9 also gives information about the initiation and propagation of the dehydrochlorination reaction. The number of unsaturation sites increased linearly. This is, in fact, in accordance with Geddes' data.[40] This increase in unsaturation sites can be explained in two ways: (1) New initiation sites are created during propagation, and (2) existing initiation sites of different thermal stability are gradually activated.

Radical transfer could explain the increase in initiation sites with conversion. However, today, most workers are of the opinion that dehydrochlorination in an inert medium at moderately high temperatures most likely proceeds via a nonradical mechanism.[7] A unimolecular initiation followed by radical propagation could also explain our results. Such a mechanism has been proposed by a Russian group.[44,45] The increase in scission sites at 0.5% conversion was about 0.2 sites per 1000 C. This content is in the order of the number of long chain branches found in PVC.[14,46,47] Such branch points are expected to have tertiary chlorine atoms—which are somewhat more stable than allylic chlorines, but are still quite susceptible to degradation.[48–50]

Although all samples were kept in an inert atmosphere, they were exposed to air for a short time while loading. It is therefore reasonable to believe that oxidation reactions may occur to a limited extent. New reactive sites can thus be formed by radical chain transfer.[16] The small decrease in molecular weight at the very beginning of the dehydrochlorination supports such a reaction (see Fig. 2). However, up to now, there is no conclusive evidence for one explanation or the other.

References

1. E. J. Arlman, *J. Polym. Sci.*, **12**, 547 (1954).
2. W. C. Geddes, *Rubber Chem. Technol.*, **40**, 177 (1967).

3. A. Guyot, J-P Benevise, and Y. Trambouze, *J. Appl. Polym. Sci.*, **6**, 103 (1962).

4. D. Braun and M. Thallmaier, *Makromol. Chem.*, **99**, 59 (1966).

5. D. Braun and M. Thallmaier, *Makromol. Chem.*, **108**, 241 (1967).

6. T. Kelen, G. Bálint, G. Galambos, and F. Tüdos, *Eur. Polym. J.*, **5**, 597 (1969).

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

8. D. Druesedow and C. G. Gibbs, *Nat. Bur. Stand., Circular 525*, Government Printing Office, Washington, D. C., 1953, p. 69.

9. M. Imoto and T. Otsu, *J. Inst. Polytechnol.*, Osaka City University Series C, **4**, 1 (1953).

10. D. K. Taylor, *Plast. Inst. Trans.*, **28**, 170 (1960).

11. B. Baum, *Soc. Plast. Eng. J.*, **17**, 71 (1961).

12. A. Guyot, P. Roux, and P. Quang Tho, *J. Appl. Polym. Sci.*, **9**, 1823 (1965).

13. J. C. Moore, *J. Polym. Sci. A*, **2**, 835 (1964).

14. K. B. Andersson and E. M. Sörvik, *J. Polym. Sci. C*, **33**, 247 (1971).

15. K. B. Andersson, Dissertation, Chalmers University of Technology, Gothenburg, Sweden, 1973.

16. K. B. Abbås and E. M. Sörvik, *J. Appl. Polym. Sci.*, **17**, 3577 (1973).

17. S. Siggia, *Quantitative Organic Analyses via Functional Groups*, 3rd. ed., Wiley, New York, 1963, p. 258.

18. K. B. Abbås and E. M. Sörvik, *J. Appl. Polym. Sci.*, **17**, 3567 (1973).

19. T. Matsumoto, I. Mune, and S. Watatani, *J. Polym. Sci. A-1*, **7**, 1609 (1969).

20. M. R. Cannon, R. E. Manning, and J. D. Bell, *Anal. Chem.*, **32**, 255 (1960).

21. L. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci. B*, **5**, 753 (1967).

22. M. Bohdanecký, K. Šolc, P. Kratochvíl, M. Kolinsky, M. Ryska, and D. Lim, *J. Polym. Sci. A-2*, **5**, 343 (1967).

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

24. E. E. Drott and R. A. Mendelson, *J. Polym. Sci. A-2*, **8**, 1361 (1970).

25. B. H. Zimm and R. W. Kilb, *J. Polym. Sci.*, **37**, 19 (1959).

26. C. D. Thurmond and B. H. Zimm, *J. Polym. Sci.*, **8**, 477 (1952).

27. A. Michel, G. Schmidt, and A. Guyot, *Amer. Chem. Soc.—Polym. Preprints* **14**, (2) 665 (1973).

28. ASTM D 2238-64T, American Society for Testing Materials, Philadelphia, 1964.

29. C. Strazielle and H. Benoit, *Pure Appl. Chem.*, **26**, 451 (1971).

30. M. Carrega, C. Bonnebat, and G. Zednik, *Anal. Chem.*, **42**, 1807 (1970).

31. B. Baum and L. H. Wartman, *J. Polym. Sci.*, **28**, 537 (1958).

32. G. A. Razuvayev, G. G. Petukhov, and V. A. Dodonov, *Vysokomol. Soedin.*, **3** (10), 1549 (1961).

33. C. Sadron, J. Parrod, and P. Roth, *C.R. Hebd. Séances Acad. Sci.*, **250**, 2206 (1960).

34. F. Sondheimer, D. Ben-Efraim, and R. Wolowski, *J. Amer. Chem. Soc.*, **83**, 1675 (1961).

35. K. W. Hausser and R. Kuhn, *Z. Phys. Chem.*, **B29**, 363 (1935).

36. F. Bohlman and H. J. Mannhard, *Chem. Ber.*, **89**, 1309 (1956).

37. D. Braun, M. Thallmaier, and D. Hepp, *Angew. Makromol. Chem.*, **2** (24), 71 (1968).

38. A. Michel, T.-V.-Hoang, and A. Guyot, *Preprints, Int. Symp. on Degradation and Stabilization of Polymers*, Brussels, September 1974, p. 17.

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

40. W. C. Geddes, *Eur. Polym. J.*, **3**, 747 (1967).

41. K. B. Abbås and R. L. Laurence, *J. Polym. Sci.—Chem. Ed.*, in press.

42. K. B. Abbås, F. A. Bovey, and F. C. Schilling, *Makromol. Chem.*, in press.

43. A. Rigo, G. Palma, and G. Talamini, *Makromol. Chem.*, **153**, 219 (1972).

44. G. A. Rasuvayev, L. S. Troitskaya, and B. B. Troitskii, *J. Polym. Sci. A-1*, **9**, 2673 (1971).

45. B. B. Troitskii, L. S. Troitskaya, V. N. Myakov, and A. F. Lepaev, *J. Polym. Sci.*, Symp. No. 42, 1347 (1973).

46. J. Lyngaae-Jörgensen, *J. Chromatogr. Sci.*, **9**, 331 (1971).

47. A. J. deVries, C. Bonnebat, and M. Carrega, *Pure Appl. Chem.*, **25**, 209 (1971).

48. M. Onozuka and M. Asahina, *J. Macromol. Sci.—Revs.*, **C3**(2), 235 (1969).

49. A. Caraculacu, *J. Polym. Sci. A-1*, **4**, 1829 (1966).

50. D. Braun and F. Weiss, *Angew. Makromol. Chem.*, **13**, 55 (1970).