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## Characterization of Polyene Sequences in Poly(vinyl Chloride)

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### ABSTRACT

Some aspects of the formation and propagation of polyene sequences during the thermal degradation of PVC have been discussed. The average polyene sequence length occurring in a suspension polymerized PVC, degraded in nitrogen at 190°C, was determined to ca. 10 units. The results were somewhat dependent on the type of analysis employed. The formation of internal polyene sequences was characterized by three stages. After an initial period, where the number of internal sites remained constant, new sites were rapidly formed. The high rate of formation then gradually decreased with increasing conversion. Degradation mechanisms explaining this behavior were suggested.

### INTRODUCTION

The discoloration of poly(vinyl chloride) (PVC) during degradation is explained by the development of conjugated double bonds (polyene sequences), which are formed through a "zipper" mechanism [1]. Discoloration occurs when the sequence length exceeds ca. five units

[2]. As the discoloration is noticeable at very low conversions, relatively long polyene sequences must be formed at the early stage of the degradation. Although there have been very much published on the degradation of PVC, we still do not know the exact details concerning the initiation, propagation and termination of polyene sequences. It is the purpose of this study to elucidate some of these reactions.

## EXPERIMENTAL

### Materials

Throughout this investigation Pevikon R-45 poly(vinyl chloride), kindly supplied by Kema Nord AB, Sweden, was used. The molecular weights were:  $\overline{M}_n = 49,000$  and  $\overline{M}_w = 113,000$ . The methyl content of the reduced sample was  $5.1 \text{ CH}_3/1000 \text{ C}$ , and the polymer contained  $0.54$  internal double bonds per  $10,000 \text{ C}$  [3].

Tetrahydrofuran was refluxed over sodium borohydride until no peroxides could be detected [4]. It was then distilled under nitrogen from metallic sodium.

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

### Dehydrochlorination Kinetics

The degradation was carried out at  $190^\circ \text{C}$  under pure nitrogen atmosphere ( $< 10 \text{ ppm O}_2$ ). A detailed description of the dehydrochlorination apparatus has been given earlier [5].

### Ultraviolet-Visible Spectroscopy

Transmission spectra of PVC solutions in THF were obtained by using a Beckman DK-2 A spectrophotometer. All PVC solutions ( $4 \text{ g/liter}$ ) were carefully prepared under an inert atmosphere and were rotated in sealed glass tubes for 4-6 hr before analysis. The solutions were to be free of peroxides and the solvent was therefore treated as discussed above (see Materials).

### Ozonation

Ca. 2 g of 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 oxygen (6 liter/hr) through passing an ozonator (Model T-23, Projecting AB, Stockholm). The gas was bubbled through the PVC suspension for 3 hr; no further decrease in molecular weight was observed after ca. 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.

### Gel-Permeation Chromatography

A Waters Associates GPC, Model 200, was used for the determination of molecular weight distributions. The experimental conditions have been given in a previous paper [6].

## RESULTS AND DISCUSSION

### Determination of the Average Polyene Sequence Length by Ultraviolet-Visible Spectroscopy

The development of polyene sequences during the thermal degradation of PVC has often been followed by ultraviolet-visible spectroscopy. It is a well known fact that transmission decreases with increasing conversion. This is demonstrated in Fig. 1.

It has been shown that every maximum in the absorption spectra could, to a good approximation, be related to a certain sequence length

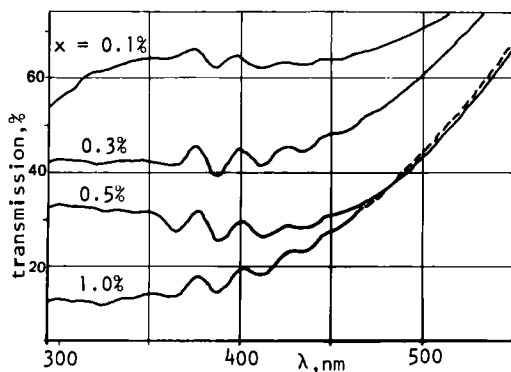


FIG. 1. Ultraviolet-visible spectra of Pevikon R-45 at different conversions. Degradation in nitrogen at 190°C.

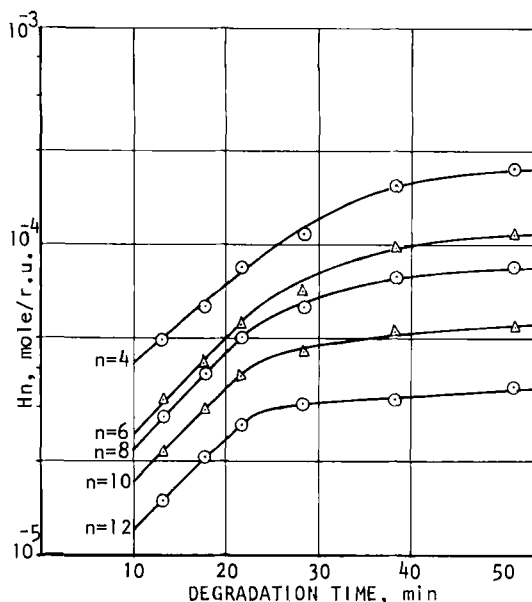


FIG. 2. Log concentration of even polyene sequence lengths as a function of degradation time for degradation of PVC in nitrogen at 190°C.

[7]. In Fig. 2 is plotted the logarithm of the polyene concentration versus degradation time. For the sake of simplicity uneven polyene sequences were excluded.

All curves are linear at the early stages, but deviate from linearity at higher conversions, which indicates the onset of secondary reactions [6]. The concentration of the polyene sequence length  $n$  was calculated from the equation,

$$H_n = (A/m)\epsilon_n$$

where  $A$  is the absorption of the examined solution at the wavelength corresponding to the polyene sequence of length  $n$ ,  $m$  is the concentration of the examined solutions in monomeric units mole/liter, and  $\epsilon_n$  is the molar extinction coefficient related to the polyene sequence length  $n$ .  $\epsilon_n$  was obtained from:  $\epsilon_n = 10,000 + (n+1) 20,000$ , where  $\epsilon_n$  is expressed in liters/mole-cm [8]. From the values of  $H_n$ , it is then possible to calculate an average polyene sequence length,  $\bar{n}$ . A value of about 6 was obtained for Pevikon R-45 [9].

Determination of the Average Polyene Sequence Length by Ozonolysis

An ozonolysis technique combined with GPC has been used to determine the average polyene sequence length. The number-average molecular weight was measured at different degrees of dehydrochlorination before and after ozonolysis [3, 6]. The amount of scission due to the breaking of double bonds was then determined. Polyene sequences may be initiated either at chain ends or in a random fashion along the macromolecule. The number of scission can be expressed by the general relationship [10]:

$$\frac{1}{\overline{DP}_n} - \frac{1}{\overline{DP}_n^0} = \frac{x - x_e}{\bar{n}} + \frac{x_e}{1 - x_e} \left( \frac{1}{\overline{DP}_n^0} \right) \quad (1)$$

where  $\overline{DP}_n$  is the number-average degree of polymerization of the ozonized polymer,  $\overline{DP}_n^0$  is the number-average degree of polymerization of the unozonized polymer,  $\bar{n}$  is the average polyene sequence length,  $x_e$  is the fractional conversion related to chain end initiation, and  $x$  is the fractional conversion corresponding to initiation within the polymer chain. As the last term in Eq. (1) is small compared to  $(x - x_e)/\bar{n}$ , Eq. (1) can be expressed as follows:

$$(1/\overline{DP}_n) - (1/\overline{DP}_n^0) \simeq (x - x_e)/\bar{n} \quad (2)$$

It is reasonable to assume that the initiation at chain ends is very limited [10], which means that  $x \gg x_e$  resulting in the following approximation:

$$(1/\overline{DP}_n) - (1/\overline{DP}_n^0) \simeq x/\bar{n}$$

The number of scissions plotted as a function of conversion should thus result in a straight line, the inverse slope of which is equal to the average polyene sequence length. Such data are depicted in Fig. 3 at two different degradation temperatures.

The average polyene sequence length was 14 at 170°C and 11 at 190°C. Using the same type of analysis, Geddes [10] found an average polyene sequence length of about 14. His degradation experiments were conducted in nitrogen at 150°C. As stated above, an analysis of ultraviolet-visible data at 190°C for the above-mentioned polymer resulted in a much lower value,  $\bar{n} \simeq 6$ .

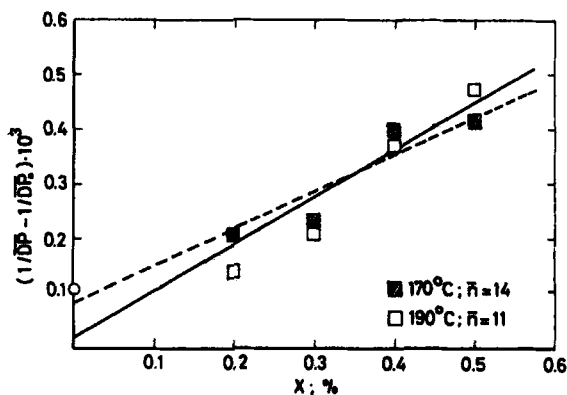


FIG. 3. Number of scissions per 1000 repetition units,  $\{(1/\overline{DP}) - (1/\overline{DP}_0) \times 10^3\}$ , during ozonolysis as a function of conversion. Pevikon R-45 degraded in nitrogen.

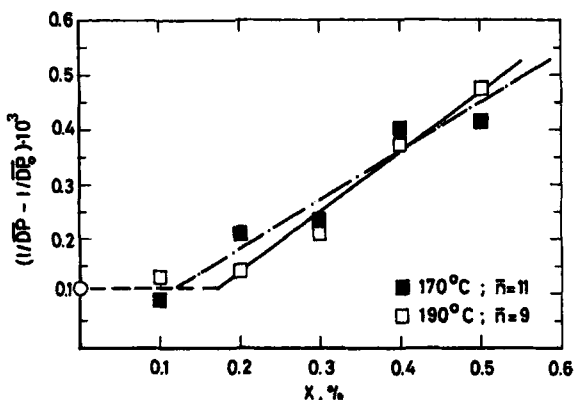


FIG. 4. Number of scissions per 1000 repetition units,  $\{(1/\overline{DP}) - (1/\overline{DP}_0) \times 10^3\}$ , during ozonolysis as a function of conversion. Pevikon R-45 degraded in nitrogen.

The straight lines in Fig. 3 have been calculated according to the least-squares method. A more detailed analysis shows that in the early stages of the dehydrochlorination, no significant change in the number of scissions is observed. Although there are few initiation sites (allylic double bonds) in the original polymer, their number is large enough to cause an appreciable degradation. Assuming an average polyene sequence length of 10 and having an initial double bond content of 0.5/10,000 C, a 0.1% conversion has to be reached before

any changes in scissions are obtained. The straight line in Fig. 3 should therefore not be affected by the values of the number of scissions at conversions up to ca. 0.1%. Figure 3 was thus replotted as shown in Fig. 4. This resulted in an average polyene sequence length of  $\bar{n} = 11$  at 170°C and  $\bar{n} = 9$  at 190°C. These values are lower than those above and more consistent with data from ultraviolet-visible measurements. In the literature, double bond contents in virgin PVC between 0.2 and 1.5 per 1000 C have been reported [11, 12]. Assuming an average polyene sequence length of 10 and an original double bond content of 0.5, which is 10 times higher than in our polymer, no change in the number of scission points are to be expected below 1.0% conversion. This implies that for such a polymer it is very difficult to obtain a value of  $\bar{n}$  by the related method.

### Initiation of Polyene Sequences

An interesting feature of Fig. 3 is the rapid increase in the number of scission sites. Similar results have been reported by Geddes [10], but without comments. However, it is important to stress the fact that the data plotted in Fig. 3 do not only give the average polyene sequence length, but also show that new polyene sequences are formed during the degradation. In Fig. 5 the data at 190°C in Fig. 3 have been completed and extended to 1.0% conversion.

The initial period is characterized by a constant chain scission, which probably corresponds to the successive activation of the allylic double bonds, originally present in the polymer. Between 0.2 and 0.6% conversion there is a rapid increase in the number of scissions indicating that new active sites are being formed. At conversions exceeding 0.6% the formation of new sequences is continuously diminished, and the number of scissions seems to approach a constant value. The total increase in initiation sites is in the order of 3 per 10,000 C. Tertiary chlorines have often been suggested as possible initiation sites. However, it was recently shown that short branches in PVC consist of pendent chloromethyl groups [13, 14], which are not exhibiting tertiary chlorines and are thus quite stable [11].

On the other hand, long branches formed through chain transfer to polymer should have tertiary chlorines at branch points and are thus more susceptible to degradation. In favor of this hypothesis is the fact that the increase in the number of initiation sites formed during the degradation is close to the content of long chain branching in the original polymer. Although the experimental accuracy is not that high, it is obvious that the growth of initiation sites decreases rapidly beyond 0.6% conversion. The number of scissions at 1.0% conversion is almost half as large as expected from a linear growth. It may be argued that a branched material reacts slower than a linear



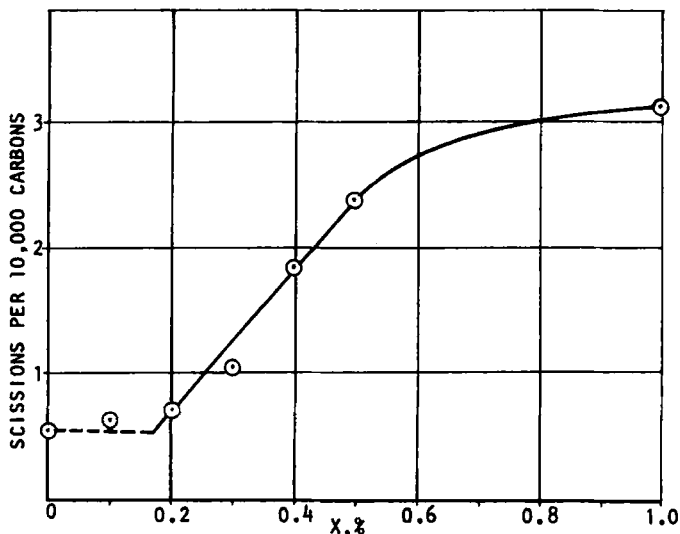


FIG. 5. Number of scissions per 10,000 carbons during ozonolysis as a function of conversion. Pevikon R-45 degraded in nitrogen at 190°C.

material and therefore needs a longer reaction time for the ozonolysis experiment. However, a PVC sample degraded beyond 1.0% conversion was tested, and it reached a limiting molecular weight before 3 hr of ozonolysis, which indicated a complete reaction.

The above results are, of course, also consistent with a radical mechanism including chain transfer. The lower increase in the number of scissions at higher conversions may, in this case, be explained by a decreasing frequency of chain-transfer reactions.

### CONCLUSIONS

The average polyene sequence length  $\bar{n}$  in thermally degraded PVC was found to be approximately 10 units. The average length decreased with increasing degradation temperature, exhibiting  $\bar{n} = 9$  at 190°C, and  $\bar{n} = 11$  at 170°C.

By using ozonolysis combined with gel-permeation chromatography, the formation of new initiation sites during dehydrochlorination was studied. The number of sites was constant at the early stages of the reaction. This indicated that only the allylic double bonds originally present in the polymer were activated. After the initial period

a very rapid increase in the formation of new sites was observed. This behavior could be explained either by radical chain transfer or initiation at labile tertiary chlorines at branch points (long branches). At conversions exceeding 0.6% the rate of formation of new sequences gradually decreased, and the number of sequences seems to approach a constant value. This could be rationalized by a decreasing tendency of radical chain transfer or the fact that most of the unstable structures are already initiated.

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## DISCUSSION

Dr. T. Kelen (Central Research Institute for Chemistry, Budapest): In one of Dr. Abbās' slides, he showed the number of polyenes determined by ozonolysis. There was a small part of the curve on which no change was observed, followed by an increase and finally a decrease in the rate of increase. Dr. Abbās said that the reason for the decreasing rate is the long-chain branching. That is, the first part of the curve refers to allylic chlorides, the last part of the long-chain

branching. In my talk I showed polyene concentrations and a similar decrease in the rate of polyene concentration increase. How does Dr. Abbås know that the last part of the curve relates to the long-chain branching?

Dr. Abbås: On the last slide I showed, there was a deviation from the linear behavior at higher conversions. This deviation can be explained if the tertiary chlorines (long branches) are successively initiated, which means that they will all be reacted) at higher degrees of conversion. I did not suggest there was conclusive evidence for this, but that this increase in the number of sites is in agreement with the number of long-chain branches in the original polymer, which was analyzed by GPC in combination with intrinsic viscosity.