

Partially Dehydrochlorinated PVC. I. Structure

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Synopsis

PVC made by suspension and anionic polymerization was partially dehydrochlorinated by three different methods. In the first one, a solution in THF and in the second one, particles swollen by dioxane were treated with alcoholic KOH at low temperatures. In the third method, a solution of PVC in DMF was heated to 130°C or refluxed (153°C). The reactions were followed by UV spectrophotometry and the products analyzed by GPC. Furthermore, the products were ozonolyzed and the molecular weights of the polymeric residues determined by GPC. Treatment with KOH in THF yielded products with randomly distributed polyene sequences. At higher degrees of dehydrochlorination a slight decrease in molecular weight was observed. The polymers were shown to be built up by PVC segments with an average degree of polymerization between 70 and 80, interspaced by polyene segments each with relatively few conjugated double bonds in sequence (fewer than 15). The reaction of KOH with particles swollen in dioxane was slower but yielded products with the same molecular structure. Thermal dehydrochlorination in DMF gave rise to long polyene sequences. They were fewer in number as evidenced by the higher molecular weights of the residues after ozonolysis.

INTRODUCTION

The tendency of poly(vinyl chloride) (PVC) to split off hydrochloric acid on heating is one of the most characteristic properties of the material. Thermal dehydrochlorination has been studied intensively, and many important features of the mechanism are known.¹ To summarize, a hydrochloric acid molecule is first split off leaving a double bond in the PVC chain. Further elimination is facilitated by the presence of allylically activated sites. The result is the formation of sequences of conjugated double bonds (polyene sequences) in the PVC chains. It has been shown by ozonolysis that the polyene sequences are more or less randomly distributed along the chains.^{2,3} They are relatively short, and the number of double bonds in them has been calculated³ to be 11–14. The polyene sequences are reactive and subject to secondary reactions resulting in crosslinking, chain scission, etc.^{3,4}

In spite of the great technological importance of PVC, only a relatively small number of reports on alkaline dehydrochlorination of the polymer have appeared after the report of Marvel et al.⁵ Some of these dealt with attempts to completely dehydrochlorinate PVC to make semiconducting polymers.^{6–11}

Bengough and Varma¹² partially dehydrochlorinated PVC in solution in THF under the influence of alcoholic KOH. The products had ultraviolet spectra similar to those obtained by thermal dehydrochlorination in solution in several solvents. The exception was DMF in which solvent long polyene sequences were obtained. Shindo and Hirai¹³ studied the kinetics and mechanism of the reac-

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tions induced by KOH. They obtained soluble polymers with degrees of dehydrochlorination of up to 8%. The rates of formation of the polyene sequences was determined by ultraviolet spectrophotometry. It was concluded that the reaction was a stepwise ionic elimination reaction. Shindo et al.¹⁴ have also studied the influence of the dehydrohalogenation on the dimensions of the PVC molecules in solution. It was found by statistical mechanical calculations and viscosimetric measurements that the hydrodynamic volume had a minimum at about 6% dehydrochlorination.

While Shindo and Hirai¹³ found low temperatures to give the fewest side reactions, Schwenk¹⁵ studied the effects of KOH and THF solutions of PVC at room temperature and at 60°C. The products were analyzed by gel permeation chromatography (GPC), and profound changes were found in the molecular weight distributions. It was concluded that both chain scission and crosslinking had occurred.

Chang and Salovey¹⁶ also studied dehydrochlorination by KOH in THF. They observed two intense Raman bands the relative intensities of which remained constant when the degree of dehydrochlorination increased. The kinetics of dehydrochlorination by KOH in THF was studied by Östensson and Flodin.¹⁷ They also found the rate of reaction to be increased very much by the addition of small amounts of dimethyl sulfoxide.

The present study was undertaken to find out the effect of varying experimental conditions on the structure of the dehydrochlorinated PVC (polyene PVC). The molecular weights were determined by GPC and the concentration and distribution of polyene segment lengths, by ultraviolet spectrophotometry. Information on the positions of the polyene segments in the PVC chains was obtained by degradation with ozone and subsequent GPC analysis. In an accompanying paper¹⁸ some reactions of the polyene PVC are reported.

EXPERIMENTAL

Materials

Suspension-polymerized PVC samples, Pevikon S, of different molecular weights were kindly provided by KemaNord AB. Before use they were twice dissolved in THF, precipitated by methanol, and dried in vacuo unless otherwise stated.

Anion PVC was made by polymerization of vinyl chloride in *n*-heptane with *t*-butyllithium as initiator.¹⁹ Tetrahydrofuran (Merck AG, pro analysi) was refluxed over sodium borohydride under nitrogen until free of peroxides and distilled immediately prior to use. 1,4-Dioxane (Merck AG, pro analysi) was stirred over activated alumina to remove peroxides and filtered immediately prior to use.

Dimethylformamide (Merck AG, pro analysi) was distilled through a Vigreux column under nitrogen immediately prior to use.

Nitrogen was purified from oxygen and water by passage over a BASF copper catalyst and subsequently through a molecular sieve (Linde, Type 4 A) column.

All other reagents used were of pro analysi grade.

Dehydrochlorination

The PVC was weighed into the reaction flask, and the occluded air was removed by evacuation and filling the flask several times with oxygen-free nitrogen. All solutions were purged before use, and all operations were performed under oxygen-free nitrogen. Three procedures were used for the dehydrochlorination reactions:

(1) **In THF.** The experimental conditions are given in Table I. The PVC was dissolved and thermostated to the reaction temperatures. An oxygen-free solution of KOH in equal parts of THF and ethanol was added to start the reaction. The samples withdrawn were precipitated in deaerated dilute HCl while being stirred. The samples were washed and kept in a large volume of distilled water for at least 24 hr, dried in vacuo over P₂O₅, and kept under nitrogen in the dark.

(2) **In Dioxane.** The experimental conditions are given in Table II. In these experiments commercial PVC was used without purification. To the thermostated suspension of PVC swollen in dioxane an oxygen-free solution of KOH in equal parts of dioxane and ethanol was added and the mixture stirred throughout the reaction. Neutralization, washing, drying, and storing were done as under (1) above. Since the PVC was in particular form throughout, the reaction precipitation was obviated.

(3) **In DMF.** The reaction conditions are given in Table III. The PVC was dissolved by heating to 60°C in about one fourth of the DMF. The solution was then diluted with the remainder of the DMF preheated to the reaction temperature. Samples were precipitated in distilled, deaerated water. Washing, drying, and storing was made as described under (1) above.

TABLE I
Reaction Conditions for Dehydrochlorinations in THF^a

Experiment no.	K value	PVC \bar{M}_n (GPC)	PVC \bar{M}_w/\bar{M}_n (GPC)	PVC, KOH, g		Ethanol, ml	THF, ml	Temp., °C
10	65	36,000	2.7	20	5.0	50	550	+5
11	65	36,000	2.7	10	2.5	25	275	+5
12	70	45,000	2.1	20	5.0	25	550	+5
13	58	32,000		10	2.5	25	275	+5
24	60	33,000	2.1	150	26.5	250	1200	+7
28	anion ¹⁹	18,000	9.7	2	0.50	5	55	+5

^a K values are those given by the manufacturer. All samples except anion PVC are commercial suspension-polymerized PVC (Pevikon-S).

TABLE II
Reaction Conditions for Dehydrochlorination in Dioxane

Experiment no.	K value	PVC \bar{M}_n (GPC)	PVC \bar{M}_w/\bar{M}_n (GPC)	PVC, g	KOH, g	Ethanol, ml	THF, ml	Temp., °C
18	70	45,000	2.1	127	8	75	360	+15
25	70	45,000	2.1	310	16	150	900	+20

TABLE III
 Reaction Conditions for Dehydrochlorination in DMF

Experiment no.	K value	PVC		PVC \bar{M}_n (viscometric) ^a	PVC, g	DMF, ml	Temp., °C
		PVC \bar{M}_n (GPC)	\bar{M}_w/\bar{M}_n (GPC)				
4	57	30,000		32,000	5.10	400	153
5	70	45,000	2.1	50,000	5.10	400	153
6	anion ¹⁹	18,000	9.7	55,000	1.50	120	153
26	60	33,000	2.1		120	1000	130
27	60	33,000	2.1		59	630	130

^a Calculated according to Danusso²⁶ after viscometric measurement of $[\eta]$ in cyclohexanone at 25°C.

^b Estimated from manufacturer's *K* value.

Ozonolysis

The procedure followed was essentially that of Geddes.² Dehydrochlorinated PVC (polyene PVC) was suspended in chloroform (150 ml) containing a few drops of methanol. Oxygen was fed through an ozone generator at 0°C, and the ozone-containing (1%–2%) oxygen gas was led into the stirred suspension of polyene PVC at room temperature for 150 min. All samples were colorless after 30 sec–15 min, depending on the degree of dehydrochlorination. The products were deswollen by methanol, evaporated, and dried in vacuo at room temperature.

Ultraviolet Spectrophotometry

The spectra were taken in a Beckman DK-2A double-beam spectrophotometer. Freshly distilled THF was used as solvent for the samples and as reference. All operations were carried out under a blanket of oxygen-free nitrogen.

From the spectra the concentrations of the polyene segments with three–ten double bonds were calculated using the absorption coefficients of Shindo and Hirai.¹³ Their method was used to calculate the number of double bonds as the molar percentage of the total number of vinyl chloride units originally present. This quantity (D_{tot}) was used as the measure of the degree of dehydrochlorination. Our analysis data indicated that side reactions, such as chemical cross-linking, were virtually absent. We therefore considered it justified to use D_{tot} as a relative measure of the degree of dehydrochlorination.

Chloride Ion Determination

Since absorption peaks due to individual polyene sequences were not resolved for the samples made by thermal dehydrochlorination in DMF, the ultraviolet spectra could not be used to determine D_{tot} in those cases. Instead, the chloride ion concentrations were determined by titration of the chloride ions with mercuric nitrate by the procedure described by Vaimann.²⁰

At higher degrees of dehydrochlorination the solutions gelled making titration of samples difficult. In those cases the degree of dehydrochlorination was given as a reaction time.

Gel Permeation Chromatography

The molecular weight distributions were determined with a Waters GPC-200 apparatus at 25°C using Styragel columns with the following exclusion limits: 5×10^6 , 7×10^5 , 1.5×10^5 , 1.5×10^4 , and 1.5×10^3 Å. The sample concentrations in all cases were 0.25% by weight.

Some of the samples, especially the low molecular weight products obtained in the analysis experiments, were rerun on a high-pressure chromatograph (Waters ALC/GPC 201) using μ -Styragel columns with the exclusion limits 10^6 , 10^5 , 10^4 , 10^3 , and 500 Å. The molecular weights obtained with both equipments were in fair agreement, although HP-GPC had a lower band spreading and a better resolution in the low molecular weight range.

The molecular weight distributions and the average molecular weights were calculated with the Q -value method²¹ after calibration with polystyrene standards of narrow distributions (Waters Assoc.). For PVC the value $Q = 25$ was used. This Q -value was also used for the dehydrochlorinated samples, which is acceptable for low D_{tot} values but become progressively more inaccurate with increasing D_{tot} values (see discussion). No corrections were made for axial dispersion.

RESULTS

Ultraviolet Spectra

In Figures 1(a), 1(b), and 4(c) the ultraviolet spectra of some typical samples of polyene PVC obtained by alkaline dehydrochlorination in THF and dioxane and by thermal dehydrochlorination in DMF, respectively, are shown. The first two methods yielded spectra composed of many relatively well-resolved peaks, while in the latter a broad absorption band was obtained. Polyenes are known to have absorption spectra composed of several peaks (for higher polyenes usually four) which are displaced toward higher wavelengths with increasing number of conjugated double bonds.²² We used the simplifying assumption that the peaks indicated in Figure 1 were due to the absorption of just one polyene sequence length each.²³ In our calculations the absorption coefficients given by Shindo and Hirai¹³ were used.

The development of the concentrations of some of the sequences in a THF dehydrochlorination as a function of D_{tot} is shown in a log-log plot in Figure 2 as was done by Abbås and Sörvik.³ At conversions below about 1% the concentration of short sequences ($n < 6$) increased at a higher rate than the longer ones ($n > 6$). However, at conversions above 1% the reverse was true. This is in contrast to the observations of Abbås and Sörvik³ for thermal dehydrochlorination. It indicates that side reactions of the long sequences were virtually absent. Note that for $n = 6$ the slope was constant throughout the reaction interval studied.

The total number of double bonds in sequences with three to ten double bonds was calculated and plotted as D_{tot} versus time. The results of some experiments with varying experimental conditions are shown in Figure 3. It is seen that the rate of double bond formation increased throughout the reactions. The molecular weight of the suspension PVC used had little influence on the rate. Anion PVC had a much lower rate of degradation, though the only obvious difference from suspension PVC was a lower degree of branching¹⁹ and a much broader

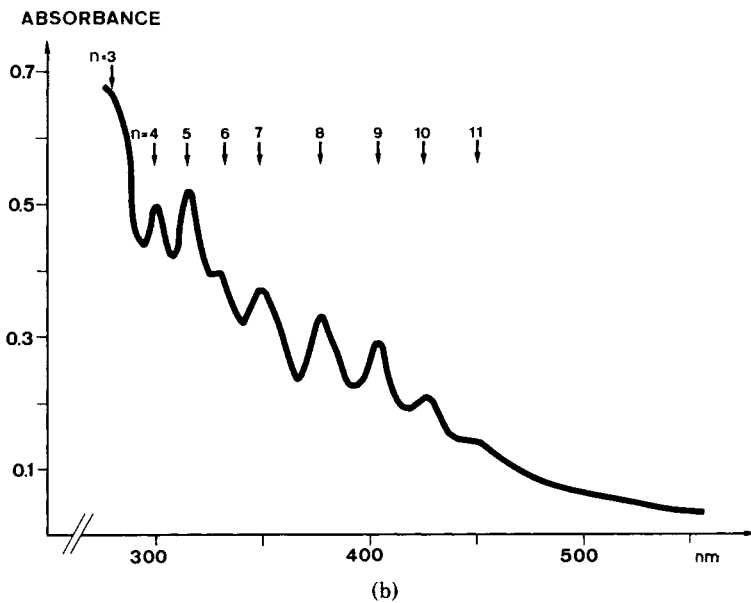
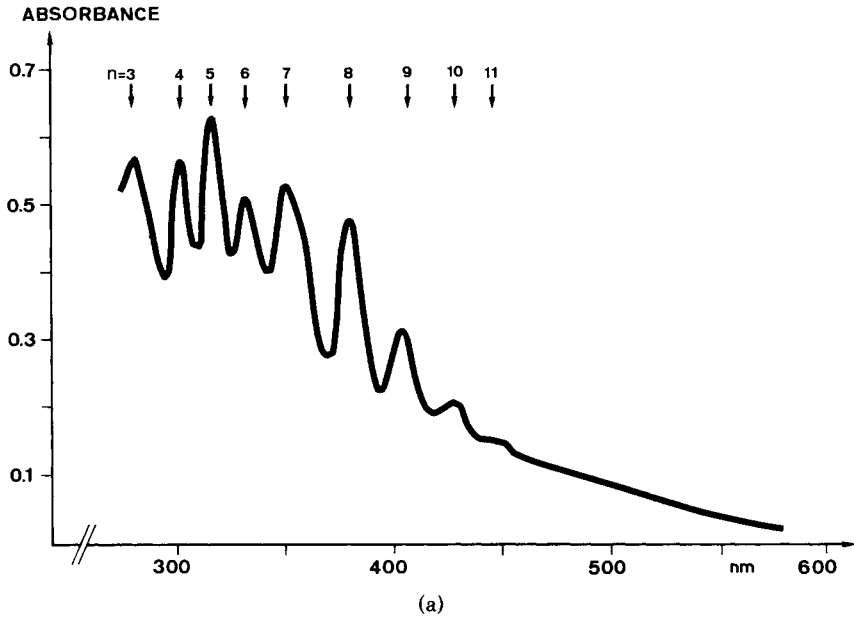


Fig. 1. Ultraviolet spectra of dehydrochlorinated PVC samples made by (a) reaction with alcoholic KOH on THF solution of PVC, experiment 12, Table I; D_{tot} , 4.1 mole-%; concentration, 0.205 g/l. (b) Reaction of alcoholic KOH with PVC beads swollen by dioxane, experiment 25, Table II; D_{tot} , 1.5 mole-%; concentration, 0.625 g/l. Number of double bonds in the polyene sequences are assigned to individual peaks as indicated.

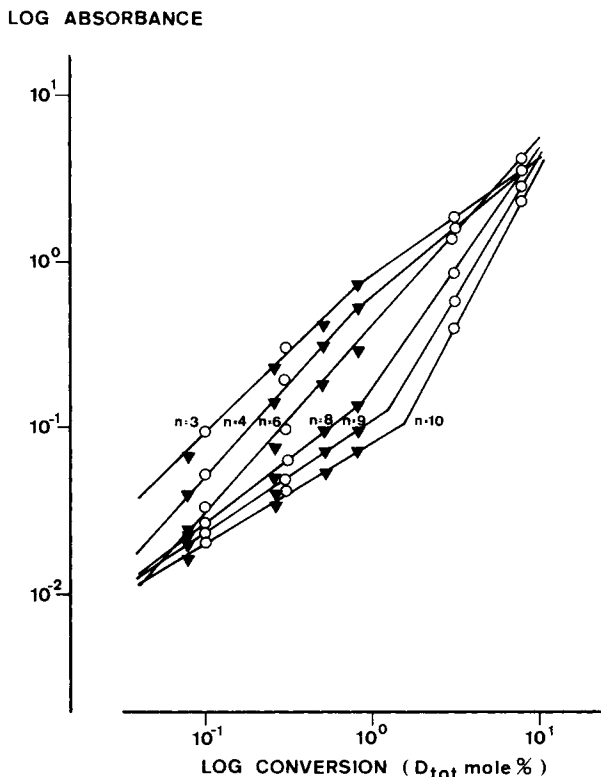


Fig. 2. Log absorbance of peaks corresponding to polyenes with n double bonds vs log conversion (D_{tot}) for dehydrohalogenation in THF solution: (O) experiment 10; (▼) experiment 11, Table I.

molecular weight distribution. This broad MWD ($HI = 9.7$) is reflected in the large difference between the \bar{M}_n values as determined by GPC and viscometry, respectively (see Table III). The dehydrochlorination of swollen PVC particles in dioxane proceeded at a much lower rate than the corresponding reaction in solution in THF. As seen in Figure 3(a), it was true even though the temperature was higher, i.e., $+20^\circ\text{C}$ versus $+5^\circ\text{C}$ in the THF solution.

The ultraviolet spectra of three samples from thermal dehydrochlorination in DMF taken at various time intervals are shown in Figure 4. In the early stages, Figure 4(a), individual peaks corresponding to short polyene sequences were observed. After longer times only a broad absorption band was present, as shown in Figures 4(b) and 4(c). In the initial stage the anion PVC had higher absorption than the suspension PVC. With progressing reaction the absorption of the latter samples was higher. Thus, the overall rate of dehydrochlorination in the degradation interval studied was higher for suspension PVC than for anion PVC. This is also evident from Figure 3(b) in which the absorbance at 450 nm was used to follow the reaction.

Gel Permeation Chromatography

Samples of polyene PVC with varying degrees of dehydrochlorination made in solution in THF and as swollen particles in dioxane were analyzed by GPC with THF as the solvent. Some typical elution curves are shown in Figure 5.

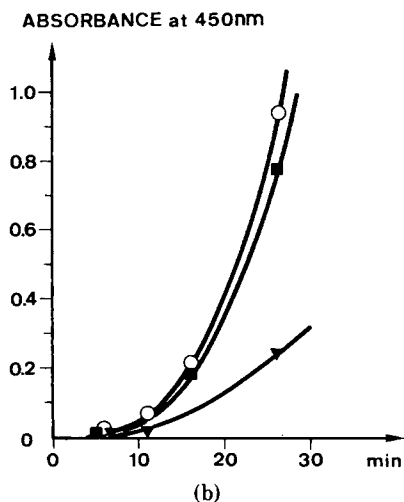
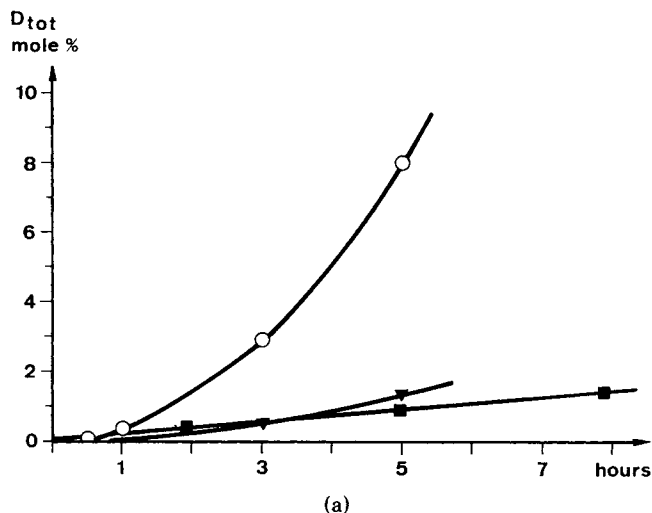


Fig. 3. (a) Total number of double bonds expressed as D_{tot} vs time: (O) suspension PVC, experiment 10, Table I; (▼) anion PVC, experiment 28, Table I, both dehydrochlorinated in THF solution at +5°C; (■) suspension PVC, experiment 25, Table II, dehydrochlorinated when swollen in dioxane at +20°C. (b) Thermal dehydrochlorination in DMF at 153°C plotted as absorbance at 450 nm vs time: (O) (■) two suspension PVC samples; (▼) anion PVC sample. Corresponding UV spectra are shown in Figures 4(a) to (c).

The samples obtained by solution dehydrochlorination were displaced toward higher elution volumes as the degree of dehydrochlorination increased. However, no signs of molecular enlargement was observed [Fig. 5(b)]. From the GPC curves the molecular weight distributions and the molecular weight averages were calculated by the Q -value method.²¹ The results are summarized in Figures 6 and 7.

In THF at 5°C (Fig. 6), the number-average molecular weight decreased and the heterogeneity index increased at higher degrees of dehydrochlorination. In

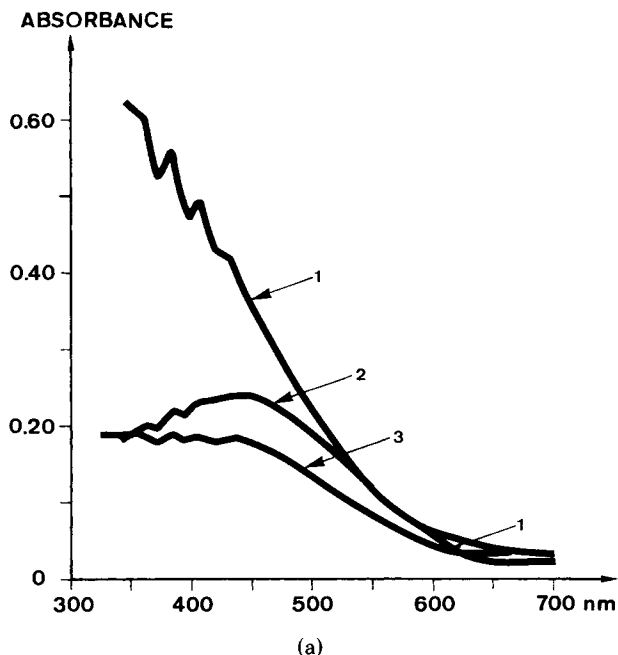


Fig. 4. Dehydrochlorination in refluxing DMF (153°C). Ultraviolet spectra in THF after (a) 6 min, concentration 10.00 g/l., (b) 11 min, concentration 3.33 g/l., and (c) 26 min, concentration 0.252 g/l. for the following PVC samples: 1, anion PVC ($M_n = 55,000$); 2, suspension PVC ($\bar{M}_n = 50,000$); and 3, suspension PVC ($\bar{M}_n = 32,000$). \bar{M}_n calculated according to Danusso²⁵ after determination of $[\eta]$ in cyclohexanone at 25°C.

dioxane (Fig. 7), no change in molecular weight was observed but a slight increase in heterogeneity. It should be observed that the molecular weights were obtained using the Q -value of PVC even for the dehydrochlorinated samples which, of course, becomes more incorrect the more the degree of dehydrochlorination increases. The decrease in hydrodynamic volume is not exclusively due to a decrease in molecular weight but may to some degree depend on lower hydrodynamic volumes of polyene PVC molecules as shown by Shindo et al.¹⁴ This effect is, however, rather small giving a maximum decrease in hydrodynamic volume of about 10% at 6% dehydrochlorination. Thus, chain scission should have the main responsibility for the decrease in molecular weight.

Thermal dehydrochlorination in DMF led to gel formation already at early stages (about 1%) of the reaction, which made analysis by GPC impossible at higher conversions. As described in an accompanying paper,¹⁸ the gels obtained in DMF could be redissolved after hydroxylation. GPC analysis of the hydroxylated gels indicated only very slight decrease in molecular weight. These GPC data are shown in Figure 7 of reference 18.

Ozonolysis

Several samples of polyene PVC were ozonolyzed to sever the polymer chains at the double bonds. The polymeric residues were analyzed by GPC. Under the conditions used, mainly the double bonds and no other groups of the polymer

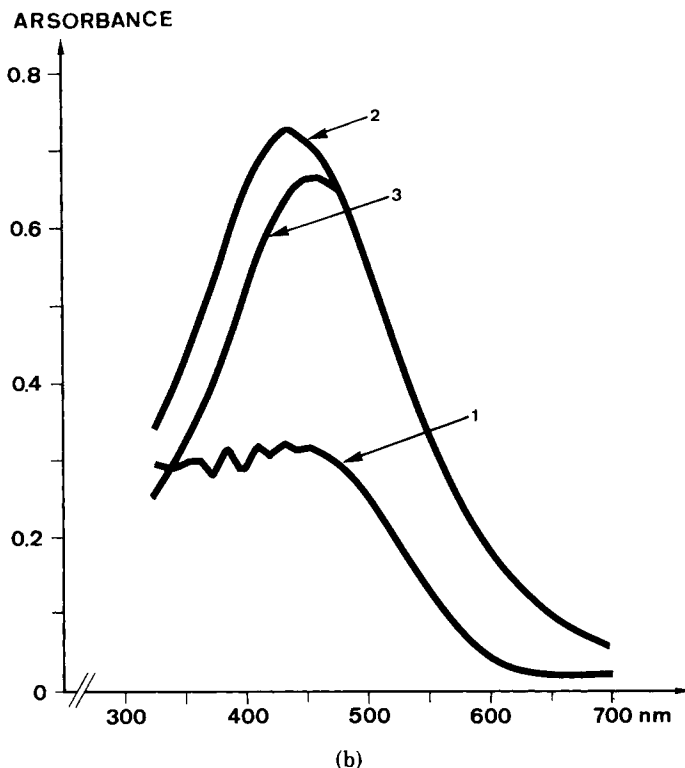


Fig. 4. (continued from previous page)

chains were attacked. The polymeric residues were assumed to be PVC with aldehyde endgroups where the ends of the polyene sequences had been situated.²⁴ In the molecular weight calculations the use of the Q -value of PVC thus seems to be justified for the ozonolyzed samples.

The results of the ozonolysis experiments are also shown in Figures 6 and 7 and summarized in Figures 8 and 9. In solution in THF, the number-average molecular weight decreased to about 4500 independent of the molecular weight of the original suspension PVC. The heterogeneity index, $\overline{M}_w/\overline{M}_n$, also decreased. It is remarkable that the molecular weights after ozonolysis were constant from about 1% to 8% (and in one experiment 16%, see Fig. 8) dehydrochlorination in the corresponding polyene PVC.

The results of ozonolysis of polyene PVC made in the swollen state in dioxane are shown in Figure 7. They are closely similar to those obtained for samples made in THF solution. This was also true for anion PVC dehydrochlorinated by KOH in THF solution in spite of the much lower rate of reaction (see Figs. 8 and 9).

Thermal dehydrochlorination in DMF, on the other hand, yielded products which upon ozonolysis gave residues with considerably higher molecular weights [Fig. 7(a) in reference 18]. They decreased, but only to a limiting value of about 14,000, compared to 4500 for alkaline dehydrochlorination.

The results of the various experiments with ozonolysis of the original PVC samples and those dehydrochlorinated by alkali are summarized in Figure 8.

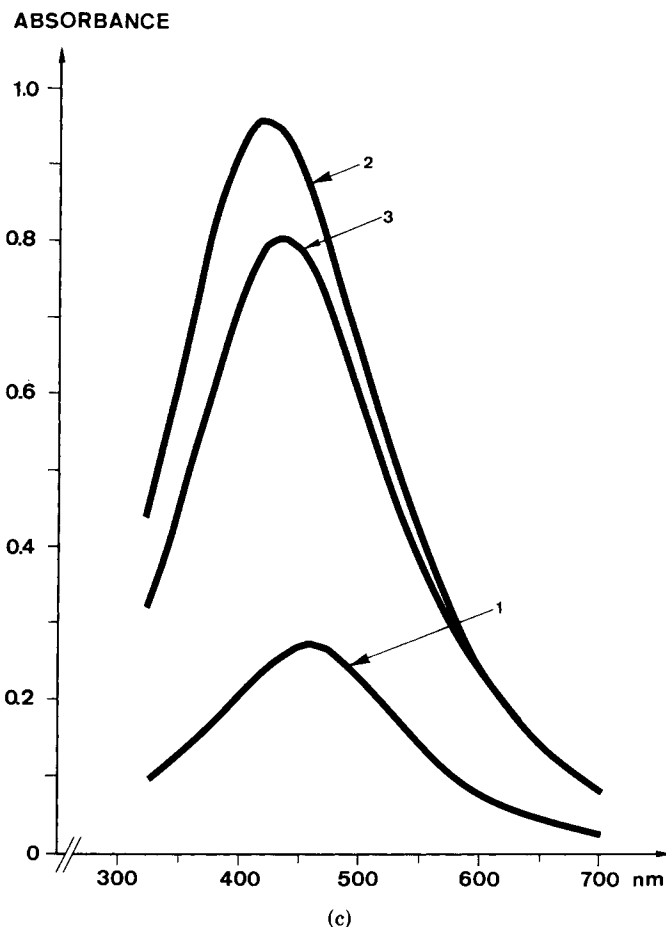


Fig. 4. (continued from previous page)

The original suspension PVC samples were not significantly affected by ozonolysis, while the original anion PVC showed a considerable decrease in \bar{M}_n . It is evident that the molecular weights of the fragments were of the same magnitude irrespective of the type of PVC and the conditions used for the alkaline degradation reaction; in all cases they approached a constant limiting value.

DISCUSSION

Dissolved in THF, PVC could be dehydrochlorinated by alcoholic KOH to moderate degrees (below about 10%) with less than one chain scission per molecule, provided the reaction was conducted at low temperature and in the absence of oxygen. At higher temperatures extensive chain scission and crosslinking reactions have been reported to occur.¹⁵ In our attempts to obtain higher degrees of dehydrochlorination (above 15%) we have found tendencies to insolubilization. If this was due to physical or chemical crosslinking is not known.

When PVC was dehydrochlorinated thermally in DMF, gelation occurred at a much lower degree of dehydrochlorination (about 1%), probably due to crys-

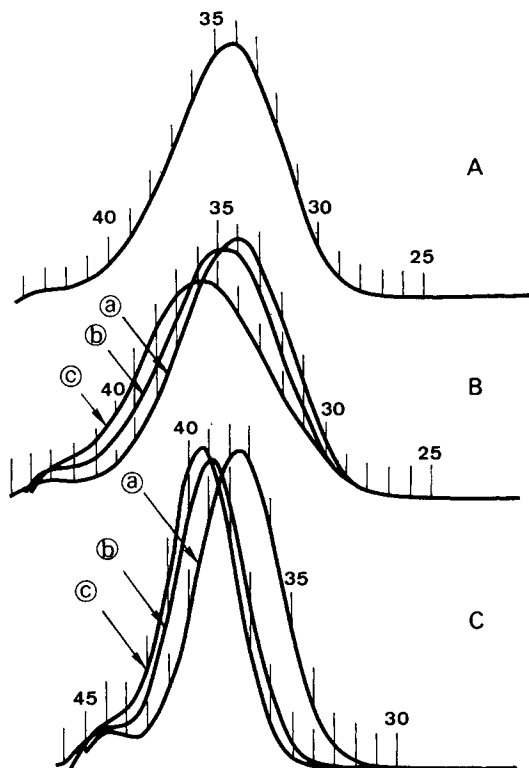


Fig. 5. GPC curves from experiment 10, Table I. A, Original suspension PVC. B, Polyene PVC after dehydrochlorination in THF for (a) 1 hr (D_{tot} , 0.3 mole-%), (b) 3 hr (D_{tot} , 3 mole-%), (c) 5 hr (D_{tot} , 8 mole-%). C, After ozonolysis of the polyene samples of B. Figures indicate counts and represent elution volume.

tallization of the comparatively longer polyene sequences obtained in this case.

Knowing that PVC could be partially dehydrochlorinated with the chain structure essentially intact, we proceeded to study the position of the polyene sequences in the molecules. This was done by ozonolysis and subsequent GPC analysis of the polymer fragments obtained. The facts that the fragments had much lower molecular weights than the original PVC and that the heterogeneity index approached the value of 2 suggest that the polyene sequences were distributed at random along the chains. It should be noted that the heterogeneity index value of 2 (Fig. 9) is expected for normal distributions in random chain scission reactions.²⁵ Both the molecular weights and the heterogeneity index approached constant values after about 1% dehydrochlorination. The same was true for both suspension and anion PVC. The results strongly suggest that the dehydrochlorination reactions were initiated at positions along the chain which were randomly distributed. Some kind of weak points introduced during synthesis in a random manner could serve as sites for initiation. The fragment molecular weight (\bar{M}_n) for the suspension PVC was about 4500 after alkaline degradation and about 14,000 after thermal degradation in DMF, which corresponds to a frequency of attack of roughly one in 150 carbon atoms in the first case and one in 450 carbon atoms in the second. This can be compared to the value of two scissions per 10,000 carbon atoms reported by Abbās and Sörvik³

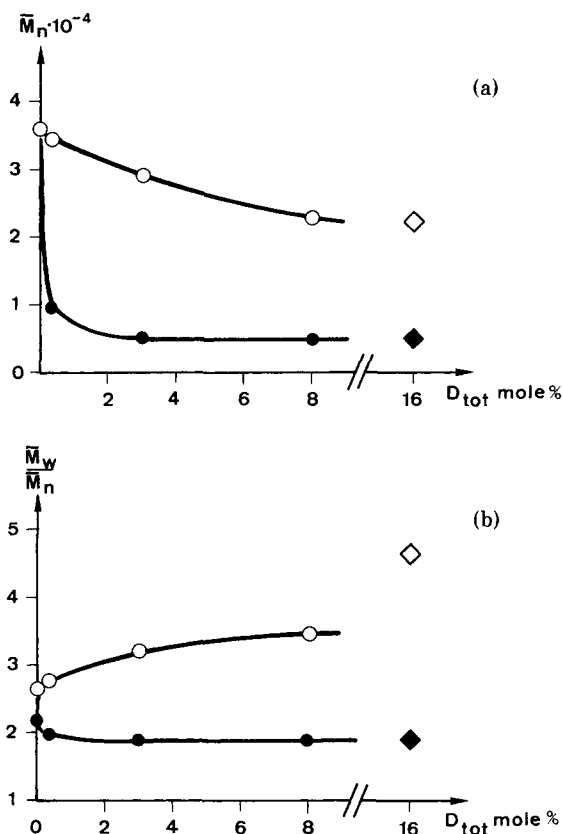


Fig. 6. Number-average molecular weights (\bar{M}_n) (a) and heterogeneity indices (\bar{M}_w/\bar{M}_n) (b) for polyene PVC made in THF solution (O) and the corresponding ozonolyzed samples (●). Curves from experiment 10, Table I: (◇) sample with $D_{tot} = 16\%$, experiment 24, Table I, reaction time 6.75 hr; (◆) the corresponding ozonolyzed sample.

for thermal dehydrochlorination in nitrogen at 0.5% dehydrochlorination, which in their case was the highest degree of dehydrochlorination achievable without crosslinking.

The ultraviolet spectra revealed that the polyene segments were short in the alkaline dehydrochlorination reactions. Few sequences had more than 15 double bonds, even at a degree of dehydrochlorination as high as 8%. Our data did not allow the calculation of the true average length of the polyene sequences since the isolated double bonds and the diene sequences were not assessed in our measurements.

As the degree of dehydrochlorination increased, the longer polyene sequences grew in number at a higher rate than the short ones (Fig. 2). This is in agreement with the results from ozonolysis that the PVC fragments had constant molecular weight after about 1% dehydrohalogenation, and thus the number of sequences did not increase after this conversion. The growth of the longer ones thus occurred at the expense of the short sequences. Upon continuing the reaction to still higher conversions, isolated double bonds and other short sequences should thus be expected to disappear. This is in contrast to what has been reported for thermal dehydrochlorination where new sites of degradation were generated throughout the reaction.^{3,28}

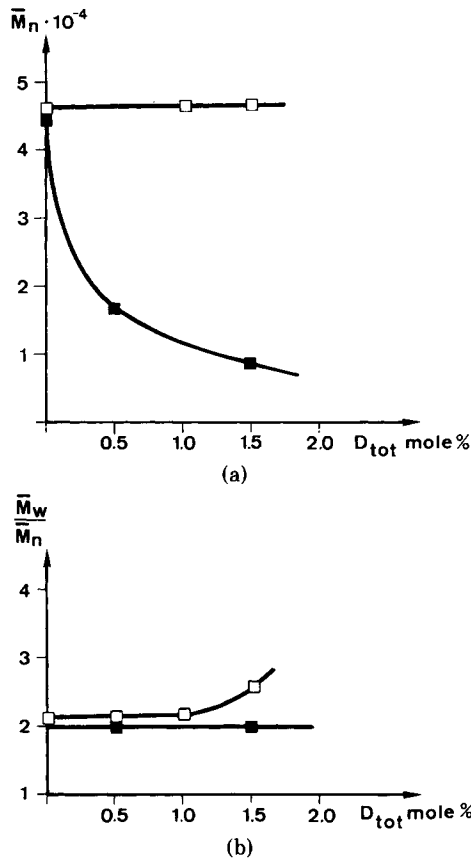
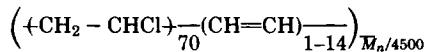


Fig. 7. Number-average molecular weights (\bar{M}_n) (a) and heterogeneity indices (\bar{M}_w/\bar{M}_n) (b) for polyene PVC samples made by alkaline dehydrochlorination of PVC beads swollen in dioxane (□) and their corresponding ozonolysis products (■). Curves from experiment 25, Table II.

Since the PVC fragments had a constant length after the first few percent of dehydrochlorination and the polyene sequences were distributed at random, the polyene PVC can be described by the formula



according to which the molecules are built up by blocks of PVC interspaced by short polyene sequences.

From a preparative point of view it was interesting to investigate other ways to dehydrochlorinate PVC than in solution. Experiments showed that little if any reaction was obtained by the action of alkali on nonswollen PVC beds. However, once they were swollen and KOH and ethanol transferred into the swollen phase, dehydrochlorination was obtained. Thus, with quaternary amines as transferring agents PVC beads swollen by benzene were dehydrochlorinated in a solution of alcoholic KOH in water. However, for the reactions reported here we chose dioxane as the swelling agent since the reaction could be performed at low temperature and thus side reactions were minimized. In this case no transferring agent was necessary since the KOH-ethanol mixture was soluble in dioxane.

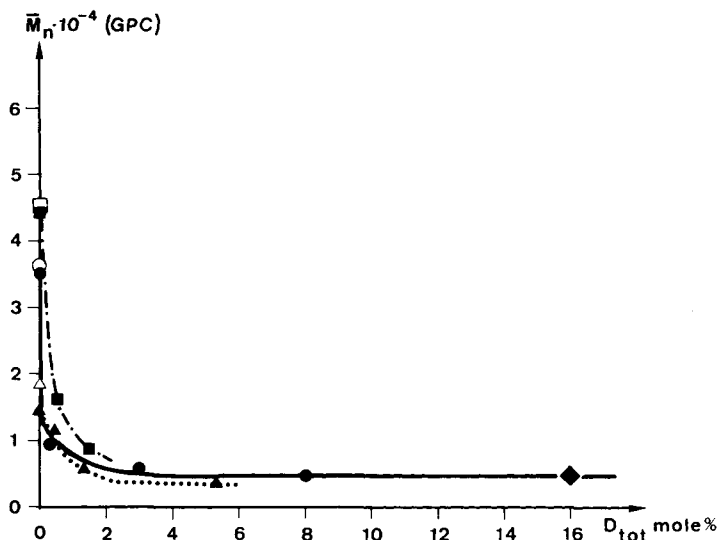


Fig. 8. Number-average molecular weights (\bar{M}_n) of ozonolysis products of PVC and polyene PVC samples: (■) suspension PVC (Pevikon S 707) dehydrochlorinated in dioxane, experiment 25, Table II; (●) (◆) suspension PVC-Pevikon S 655 dehydrochlorinated in THF, experiments 10 and 24, Table I; (▲) anion PVC¹⁹ dehydrochlorinated in THF, experiment 28, Table I. Unfilled symbols designate original PVC.

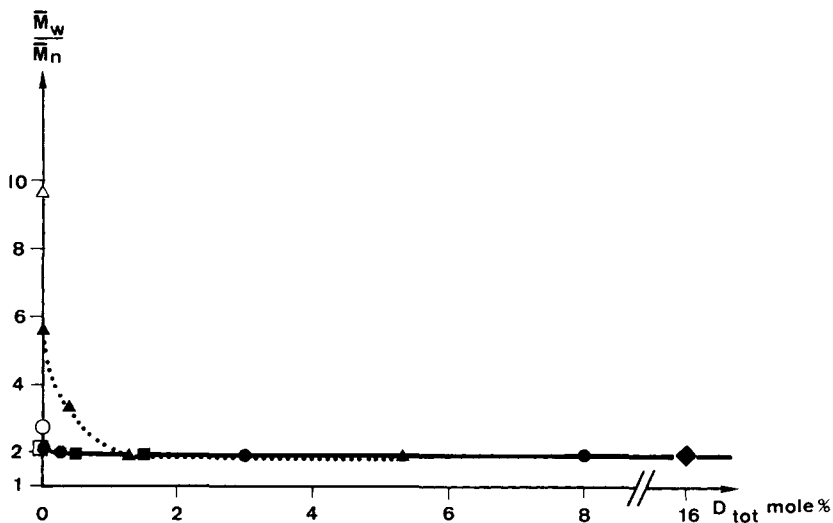


Fig. 9. Heterogeneity index \bar{M}_w/\bar{M}_n for PVC fragments obtained by ozonolysis of polyene PVC whose degree of dehydrochlorination is expressed by D_{tot} (mole-%): (■) suspension PVC-Pevikon S 707 dehydrochlorinated in dioxane, experiment 25, Table II; (●) (◆) suspension PVC-Pevikon S 655 and 602 dehydrochlorinated in THF, experiments 10 and 24, Table I; (▲) anion PVC¹⁹ dehydrochlorinated in THF, experiment 28, Table I. Unfilled symbols designate original PVC.

As shown in Figure 9, dehydrochlorination in dioxane yielded PVC blocks of the same size as was obtained when the reaction was performed in solution in THF. Also similar ultraviolet spectra were obtained and thus distributions of polyene sequence lengths. It was concluded that the polyene PVC from the reaction of KOH with PVC swollen by dioxane had a closely analogous structure.

The presence of crystalline regions and the steric effect expected from them apparently had little effect on the course of the reaction. This may be due to the fact that the syndiotactic sequences responsible for crystallinity do not participate in the dehydrochlorination reactions, at least at low conversions.

The rate of dehydrochlorination was impractically low in dioxane even at 20°C, at which temperature the reaction could be performed without change in molecular weight. It has been shown, however, that the rate of reaction can be increased very much by the addition of dimethyl sulfoxide to the solvent.¹⁷

Bengough and Varma¹² studied dehydrochlorination of PVC at elevated temperatures in a number of solvents. They concluded that most solvents gave similar products with relatively short polyene sequences. However, dimethylformamide was an exception. Upon heating a solution of PVC in DMF, long polyene sequences were obtained. We were able to confirm their results and extended them by subjecting the products to ozonolysis and subsequent GPC analysis. The polymeric residues had number-average molecular weights of about 14,000, i.e., about three times the molecular weights obtained after alkaline dehydrochlorination and subsequent ozonolysis. Even in this case all the sequences were formed at low conversions and no new ones were formed beyond about 1% dehydrochlorination. It thus seems as if the reaction in DMF was initiated at only one third the number of sites when compared to the alkaline dehydrochlorination. A possible explanation is that different sites are activated in the two types of reaction. Another explanation is that there are two different types of sites one of which can be activated by both alkali and hot DMF and the second type can only be activated by alkali.

At a degree of dehydrochlorination of about 1%, the DMF solution gelled and the products from higher conversions were insoluble in all solvents tried. Obviously, they were crosslinked either physically or by covalent bonds. The fact that ozonolysis yielded soluble products proved that the polyene sequences were responsible for the insolubilization. As shown in another paper,¹⁸ hydroxylation of the polyene PVC from thermal dehydrochlorination in DMF resulted in products soluble in THF and having nearly the same GPC curve as the original PVC. The implication is that the crosslinks were of a physical nature and due to crystallization of the polyene sequences. Since such gel formation was not observed for polyene PVC made by alkaline dehydrochlorination, the length and/or the configuration of the polyene sequences were the determining factors.

We know that longer sequences were obtained in DMF, and it thus seems justified to assume that a certain minimum length of the sequences must be exceeded before crystallization can occur. In this connection it should be mentioned that alkaline dehydrochlorination to more than 15%–20% under carefully controlled conditions also frequently gave rise to gel formation.

Steric conditions as well as polyene sequence length interfere, as shown in reference 8, where soluble polymers were obtained after extensive dehydrochlorination in DMF if part of the chlorine in the original PVC had been replaced by diphenylmethyl groups. In this case,⁸ the dehydrochlorination was carried out in the presence of lithium chloride, which is a strong base in DMF.

As mentioned above, in both alkaline and thermal dehydrochlorination anion and suspension PVC gave polyene PVC products of similar structure. However, the rates of reaction were much lower for anion PVC under all comparable conditions tried. The similarity of the fragments after dehydrochlorination and

ozonolysis indicates that the reactions were initiated at similar sites. The fact that anion PVC had a lower degree of chain branching¹⁹ did not seem to have any significant influence on the location and number of initiation sites. However, the growth of the polyene segments seemed to proceed at a lower rate as compared to suspension PVC. This is in accordance with the observation of Geddes²⁷ for a PVC sample with a low degree of chain branching. Some other structural feature, such as a different microstructure, might explain the lower rates of the polyene growth reactions. However, NMR studies of the same samples did not reveal such differences in microstructure that might be the cause of the rate differences.¹⁹

Another noticeable difference in behavior between anion and suspension PVC is the relatively large decrease in molecular weight and heterogeneity index after ozonolysis of virgin anion PVC, as seen in Figures 8 and 9, respectively. This indicates a higher amount of weak sites, possibly double bonds, in the virgin anion PVC. As a consequence, the limiting average molecular weight value after dehydrochlorination and ozonolysis is somewhat lower than for suspension PVC, which is also evident from Figure 8. Of course, this does not mean that initiation sites have to be present as isolated double bonds from the beginning. This is clearly illustrated by the fact that suspension PVC is quite unaffected by ozonolysis before dehydrochlorination. Besides, the molecular weight of virgin anion PVC after ozonolysis is still much higher than the limiting molecular weight.

The lower limiting value for anion PVC should also be a result of the broad MWD of anion PVC, which already from the beginning provides a higher content of very low molecular weight PVC compared to the suspension PVC samples as shown by GPC curves.

CONCLUSIONS

We have observed that for all dehydrochlorinations studied a limiting number of polyene sequences is reached after a certain degree of dehydrochlorination, as indicated by a limiting molecular weight after subsequent ozonolysis as well as by kinetic studies of the dehydrochlorination. This seems to be valid up to rather high degrees of dehydrochlorination.

The limiting value and average sequence length depend on reaction conditions and to some extent on the MDW and possibly the content of double bonds in the original PVC.

The heterogeneity index after a certain degree of dehydrochlorination and subsequent ozonolysis was close to the value of 2, regardless of the type of PVC, molecular weight, and method of dehydrochlorination. This indicates that the polyene sequences are randomly distributed in the chain after dehydrochlorination.

This work was supported by grants from the Swedish Board for Technical Development (STU).

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Received October 10, 1977

Revised February 15, 1978