

Formation of anomalous structures in PVC and their influence on the thermal stability: 3. Internal chloroallylic groups*

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Internal double bonds were determined by oxidative cleavage in fractions of a commercial suspension PVC (S-PVC) and experimental PVC samples obtained at subsaturation conditions (U-PVC). The changes in molecular weight were measured by g.p.c. and viscometry. The oxidation was performed by ozonolysis in tetrachloroethane solution at -20°C . Oxidation by potassium permanganate in dimethylacetamide solution at -10° to $+50^{\circ}\text{C}$ was also studied. However, this method was found to give erratic results. With increasing monomer starvation the number of internal double bonds increased. In the original S-PVC sample the internal double bond content was 0.2/1000 VC. The formation of double bonds is assumed to be the result of an increased tendency, by chlorine atoms, to attack on the methylene groups in the chain. Hydrolytic cleavage and ^1H n.m.r. measurements did not give any evidence of ketoallylic groups. With increasing chloroallylic group content the U-PVC samples showed an increased rate of dehydrochlorination at 190°C in nitrogen. The S-PVC fractions, however, showed a decreased rate. However, the thermal stability in both series of samples could be related to the tertiary chlorine content. Butyl and long chain points with tertiary chlorine are more frequent than the internal chloroallylic groups. It was assumed that tertiary chlorine is the most important labile structure not only in U-PVC but also in ordinary PVC.

Keywords Poly(vinyl chloride); thermal stability; internal double bonds; allylic chlorine; tertiary chlorine; ozonolysis

INTRODUCTION

In a series of investigations we have determined different irregular structures in PVC and evaluated their effect on thermal stability. We have compared fractions of a commercial suspension PVC (S-PVC) with polymers prepared at reduced monomer pressure, subsaturation PVC (U-PVC). With decreasing monomer pressure the U-PVC showed decreased thermal stability and molecular weight. In the S-PVC series there was only a weak relationship between molecular weight and the rate of dehydrochlorination.

The first paper² in this series was mainly concerned with an investigation of end group structures by n.m.r. spectroscopy. It was shown that the most frequent unsaturated end group in S-PVC is $\sim\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$ (~ 0.7 per molecule). The most frequent saturated end group is $\sim\text{CHCl}-\text{CH}_2\text{Cl}$ ($\sim 0.8-0.9$ per molecule). Neither of these end groups have any influence on the thermal instability to any appreciable extent. In U-PVC the relative content of 1-chloro-2-alkene end groups decreases with decreasing monomer pressure while the concentration of 1,2-dichloroalkane end groups seems to be constant. We also found $\sim\text{CH}_2-\text{CH}_2\text{Cl}$ end groups, increasing with the monomer starvation at polymerization.

The present investigation concentrates on internal structures, as we considered them to be the major cause of the decreased thermal stability of U-PVC. The second paper³ in our series was concerned with branch structures in S-PVC and U-PVC. The analysis was made using ^{13}C n.m.r. after reductive dehalogenation by tributyltinhydride. To reveal the position of chlorine in the original PVC, reductions were also performed with tributyltindeuteride. It was shown that the amount of butyl and long chain branching (LCB) increased with decreasing monomer pressure at polymerization. The presence of LCB in U-PVC, as determined by g.p.c.-viscometry, has previously been reported⁴⁻⁶. Also in the S-PVC polymers a small content of butyl and/or long chain branching could be detected. The measurements on the deuteride reduced samples showed that the butyl branch points and the major part of the long chain branch points contained tertiary chlorine. The tendency to dehydrochlorination could be correlated to the content of tertiary chlorine.

The formation of butyl branches was suggested as a result of 'back-biting' while the long chain branches should be formed after hydrogen abstraction from polymer chains by macroradicals and chlorine atoms. The latter are now believed to be the actual transfer agent in the ordinary transfer to monomer^{1,2,7,8}. We also suggested that formation of internal double bonds was

* Part of a paper (ref. 1) presented at the Third International Symposium on Poly(vinyl chloride) in Cleveland, USA, August 1980.

Table 1 Comparison between ozonolysis and KMnO_4 treatment

Reaction conditions	$C=C_{\text{int}}/1000 \text{ VC}$	
	A3	C-7
Ozone, -20°C	0.92	0.25
KMnO_4 , 50°C ,	0.96	0.65
KMnO_4 , 30°C	0.62	0.37
KMnO_4 , 10°C	0.41	0.08
KMnO_4 , -10°C	—	0.05

possible after an attack of chlorine atoms on polymer chains.

In this paper we present the results of our studies on internal unsaturation in the S-PVC and U-PVC samples. The analysis of these structures was made by measuring \bar{M}_n with g.p.c. and viscometry before and after oxidative cleavage of double bonds. Both potassium permanganate and ozone were tested as oxidative agents but ozone was mainly used.

EXPERIMENTAL

Materials

The same polymer samples were used as in the previous investigations^{2,3}. The U-PVC samples were polymerized at 55°C and at monomer pressures between 59–92% saturation pressure at 55°C , (Table 1, ref. 3, previous paper). The fractions of S-PVC were obtained by extraction at 25°C from a commercial S-PVC (Pevikon S-687, KemaNord AB, Sweden) polymerized at 55°C , (Table 2, ref. 3, previous paper).

Molecular weights and LCB

Gel permeation chromatography (g.p.c.) and viscometry were used for determination of molecular weight distribution (*MWD*) and LCB. Details of the g.p.c. analysis and viscometry measurements have been given previously⁹. Intrinsic viscosity was determined in tetrahydrofuran at 25°C with an Ubbelohde viscometer. No correction for kinetic energy losses was necessary. A Waters Associates GPC Model 200 operating at 25°C with tetrahydrofuran as solvent was used. The column combination consisted of 5 Styragel columns with permeabilities ranging from 10^3 to 10^7 \AA , giving good separation in the molecular weight range of particular interest. To calculate *MWD*, molecular weight averages and LCB the computer program devised by Drott and Mendelson¹⁰ was used, assuming trifunctional branch points. The calibration for linear PVC was obtained via the universal calibration curve described elsewhere⁹.

Oxidative treatment

The treatment with KMnO_4 was performed according to Braun and Quarg¹¹. PVC (1 g) was dissolved in *N,N*-dimethylacetamide (100 ml) and KMnO_4 (0.2 g) in *N,N*-dimethylacetamide (100 ml) was added. The solution was kept at the reaction temperature (-10° to $+50^\circ\text{C}$) up to 100 h. Samples were withdrawn periodically. Excess KMnO_4 and manganedioxide formed were reduced by adding formic acid (4 ml) and heating to 75°C . The polymer was precipitated and washed with methanol. Finally the sample was dried in vacuum for 24 h.

The treatment with ozone was performed according to Michel *et al.*¹² PVC (1 g) was dissolved in tetrachloroethane (200 ml) and methanol (2 ml) was added. The solution was thermostatically controlled at -20°C . Ozone was generated by leading oxygen (61/h) through an ozonator (Model T-23, Projecting AB, Stockholm). The gas was bubbled through the solution for 2 h. The polymer was then recovered by precipitation in methanol and was dried in vacuum for 24 h.

The internal double bond content ($C=C_{\text{int}}$) was calculated from the number average molecular weight before and after the oxidative treatment:

$$C=C_{\text{int}}/1000 \text{ VC} = (1/\bar{M}_n - 1/\bar{M}_{n,0}) \cdot 62500 \quad (1)$$

where $\bar{M}_{n,0}$ is the original number average molecular weight and \bar{M}_n the number average molecular weight after ozonation.

RESULTS AND DISCUSSION

Allyl activated chlorine has long been considered the most important labile structure in PVC (see e.g. refs.13 and 14). Experiments with low molecular weight models have shown that an allylic chlorine along the chain is much more labile than a similar structure at the chain end¹⁵. Apart from this generally accepted conclusion the agreement about content and effect of internal allylic chlorine in PVC is rather poor. A major reason is the difficulty in determining this structure accurately as the content is low.

No specific analytical method exists for determining internal allylic chlorine. Instead an indirect value is obtained by determining the amount of internal double bonds. The latter method is based on oxidative cleavage of all unsaturated structures and measuring the decrease in \bar{M}_n . In this way only double bonds situated far enough from the chain ends will be determined. If \bar{M}_n can be determined with an accuracy of 2% the number of internal double bonds will be, as a result, 4% too low, assuming a random distribution. At a very low content of double bonds the relative error will increase sharply due to the increased influence of the relative error in the \bar{M}_n determination¹⁶.

Normally, molecular weights of PVC are determined by viscometry. To be able to use equation (1) the value of intrinsic viscosity is converted to \bar{M}_n by a suitable Mark-Houwink relation. However, this assumes that the width (e.g. \bar{M}_w/\bar{M}_n) of the molecular weight distribution (*MWD*) is known. In most cases \bar{M}_w/\bar{M}_n is considered to be equal to 2 and it is further assumed that this value does not change during the oxidative treatment. These assumptions are not always valid. As the \bar{M}_w/\bar{M}_n value of U-PVC is increasing with decreasing pressure⁶ we have chosen to work with g.p.c. for the \bar{M}_n determination. Another advantage with this technique is that the accuracy does not decrease with decreasing molecular weight.

Ozone is the most commonly used oxidizing agent^{12,16-25} but the use of potassium permanganate has also been reported^{11,22,26}. In the earlier work with ozone, a constant viscosity after a certain reaction time was taken as a proof that cleavage had occurred at the double bonds only¹⁷⁻¹⁹. Michel *et al.*^{12,21} have made more detailed studies on the ozonation. Working in solution they found

Table 2 Changes in \bar{M}_n and \bar{M}_w for sample C-7 during KMnO_4 treatment at 30°C

Reaction time (hours)	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	\bar{M}_w/\bar{M}_n
0	44.7	96.4	2.15
1.5	41.3	89.5	2.16
7	35.5	76.8	2.16
23	29.8	69.5	2.33
30	30.0	82.5	2.75
48	30.3	84.1	2.78

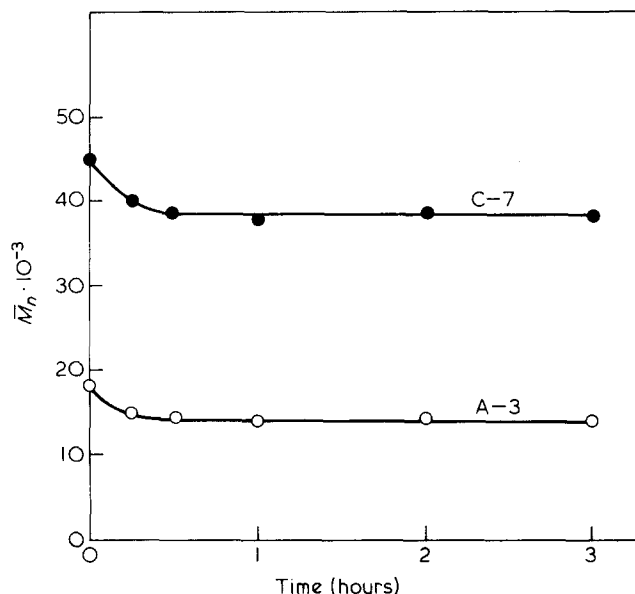


Figure 1 Changes in \bar{M}_n with oxidative treatment with ozone in tetrachloroethane solution at -20°C ; \circ , U-PVC, sample A3; \bullet , S-PVC, sample C-7

When considering which oxidizing agent should be used, we decided to first make a comparative investigation with one U-PVC and one S-PVC sample (A3 and C-7, respectively). The rate of dehydrochlorination of sample A3 is about 4 times higher than that of sample C-7 (Tables 1 and 2, part 2, previous paper). If internal unsaturation is the major cause of the low thermal stability, the U-PVC sample should have a much higher abundance of such structures.

The earlier work at our laboratory with ozonolysis was performed in a chloroform suspension at room temperature^{23,24}. However, in order to overcome diffusion problems the ozonolysis experiments in this

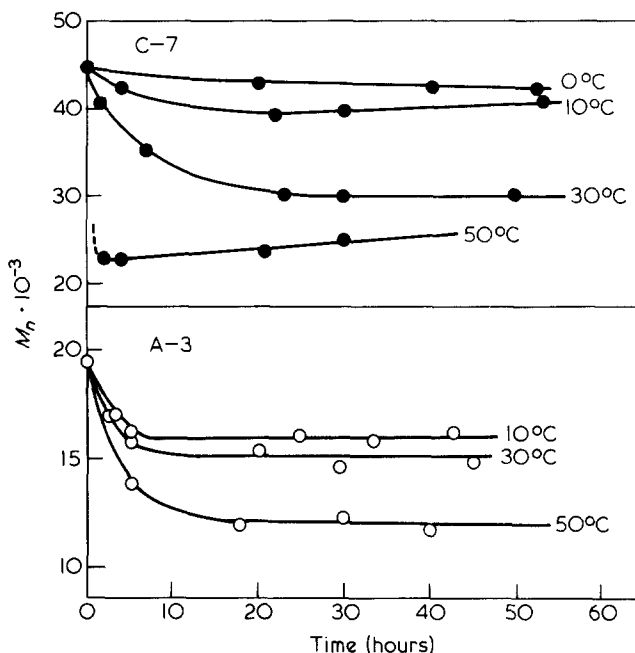


Figure 2 Changes in \bar{M}_n with oxidative treatment with KMnO_4 in dimethylacetamide solution at -10 to $+50^\circ\text{C}$; \circ , U-PVC, sample A3; \bullet , S-PVC, sample C-7

that the molecular weight was continuously decreasing at temperatures between 0° – 120°C . However, at -20°C a constant value was obtained after about half an hour. They considered that ozone only reacts with double bonds and that no other cleavage reactions take place at this temperature. A constant molecular weight has also been reported after 2 h ozonation in a chloroform suspension^{23,24}. The concentration of internal unsaturation in normal PVC obtained by ozonolysis has been reported to be 0 – $0.5/1000 \text{ VC}$ ^{12,23–25}.

Braun and Quarg¹¹ found that a constant molecular weight was also obtained when KMnO_4 was used as the oxidizing agent. The same plateau was obtained in the temperature range 20° – 70°C but the time to reach constant molecular weight depended greatly on the temperature (about 2 h at 70°C to 120 h at 20°C). In his investigation into the KMnO_4 method Lindenschmidt²² found approximately the same behaviour. However, he also found that the number of cleavages was markedly dependent on the concentration of KMnO_4 and that the chlorine content was decreasing with reaction time. He therefore did not consider KMnO_4 to be a specific reagent for double bonds in PVC. The values reported^{11,22,26} for the KMnO_4 method, 0.2 – $3.5/1000 \text{ VC}$, are generally higher than those obtained by ozonolysis.

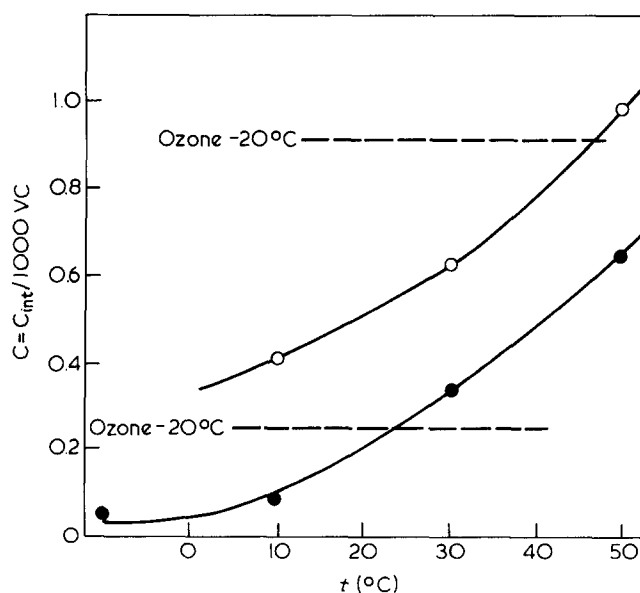


Figure 3 Number of internal double bonds calculated according to equation (1) as a function of the reaction temperature during KMnO_4 treatment; \circ , U-PVC, sample A3; \bullet , S-PVC, sample C-7

Table 3 Content of internal double bond in the U-PVC and S-PVC samples

U-PVC		S-PVC	
Sample no.	$\frac{C=C_{int}}{1000 VC}$	Sample No.	$\frac{C=C_{int}}{1000 VC}$
A 1	0.96	C-3	0.04
A 2	0.78	C-4	0.06
A 3	0.92	C-5	0.16
A 4	0.64	C-6	0.14
A 5	0.82	C-7	0.25
A 6	0.54	C-8	0.30
A 7	0.88		
A 8	0.70		
A 9	0.56		
A10	0.42		

investigation were made in solution. Considering the study made by Michel *et al.*^{12,21} we performed the ozonolysis at $-20^{\circ}C$. The changes in \bar{M}_n with reaction time for samples A3 and C-7 are shown in Figure 1. For both samples \bar{M}_n is dropping rapidly in the first 15 min and after 30 min no further decrease can be seen. As expected the amount of internal double bonds is higher in the U-PVC than in the S-PVC, (see Table 1).

The molecular weight also decreased to a constant value when $KMnO_4$ was used as the oxidizing agent, but the time to reach the plateau was longer and increased with decreasing temperature (see Figure 2). In contrast with earlier reported investigations^{11,22} the molecular weight was increasing with decreasing temperature. The number of internal double bonds was decreasing to values well below those obtained by ozonolysis, (see Table 1 and Figure 3).

Another observation made in the experiment with $KMnO_4$ is that the molecular weight tends to increase after some time (see e.g. C-7, $50^{\circ}C$, Figure 2). This is more clearly observed if the \bar{M}_w values are considered, see e.g. in Table 2 where the molecular weight data for the $KMnO_4$ treatment of sample C-7 at $30^{\circ}C$ is given. Clearly, a crosslinking reaction counteracts the oxidative cleavage resulting in a broadening of the *MWD*. Considering these results and those obtained by Lindenschmidt²² $KMnO_4$ cannot be considered as a specific reagent for cleavage of double bonds in PVC. We therefore used ozonolysis for the determination of internal unsaturation in the other samples.

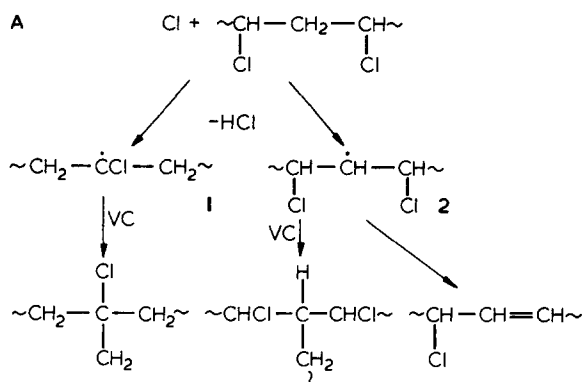
In Table 3 the number of internal double bonds is given. Although the data are rather scattered there is a clear tendency towards higher degrees of internal unsaturation with decreasing monomer pressure at the polymerization (see Figure 4). The scatter of the data partly reflects the relatively high uncertainty of the method (about $\pm 20\%$). Furthermore, it is likely that the monomer concentration in some of the subsaturation polymerizations was somewhat lower than expected from the monomer pressure. The polymerizations might have been diffusion controlled, e.g. due to particle aggregation²⁷. The precise influence of monomer pressure as well as polymerization temperature on the formation of internal double bonds is now being studied with polymers prepared under accurately controlled conditions²⁸.

The content of internal double bonds in the S-PVC series increases with increasing molecular weight. The

same, as well as the opposite behaviour was observed by Burille¹⁶ for fractions of bulk polymerized PVC.

The observed increase of internal unsaturation with decreasing monomer pressure is difficult to explain with the mechanisms suggested for the formation of double bonds within the PVC chains. A certain amount of random thermal dehydrochlorination is supposed to occur during polymerization²⁹. Braun and Sonderhof³⁰ have shown that the presence of oxygen will increase the amount of internal unsaturation. Based on model experiments Caraculacu *et al.*³¹ have suggested that alkyne impurities in the monomer will produce unsaturation in the polymer chain by copolymerization. None of the suggested mechanisms would, however, lead to an increased amount of internal double bonds at decreasing monomer pressure.

At the PVC symposium in Cleveland¹ we suggested a mechanism based on an unselective attack of chlorine atoms on the polymer chain which e.g. results in the formation of internal double bonds:



The presence of chlorine atoms is one result of an occasional head-to-head addition during propagation^{1,2,7,8}:

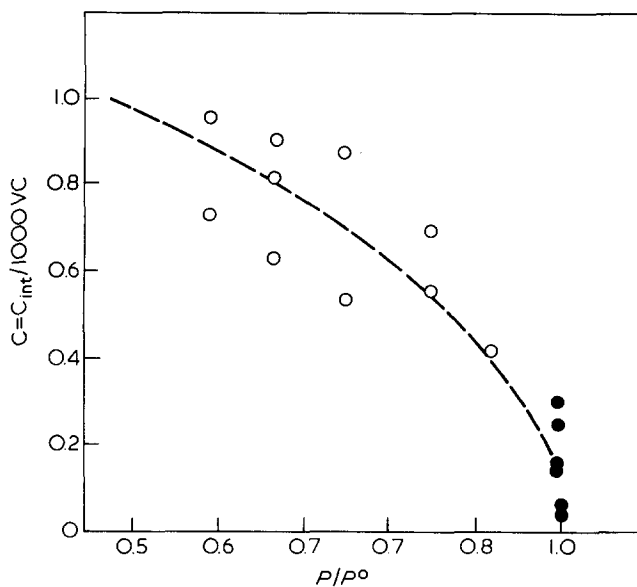
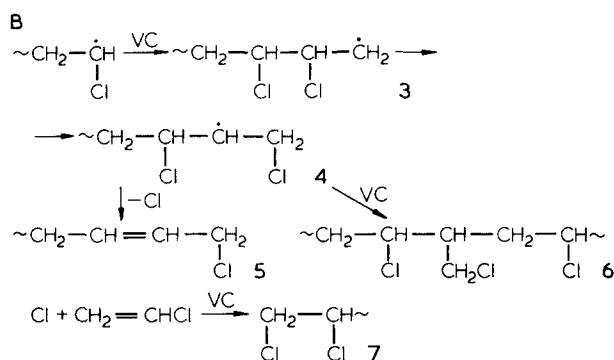
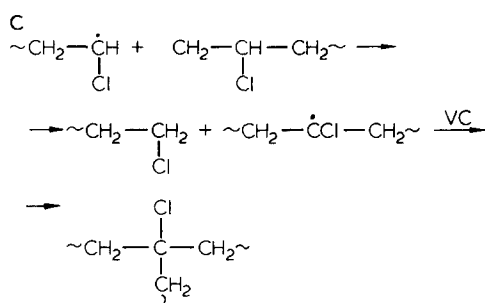


Figure 4 Amount of internal double bonds per 1000 VC as a function of the relative monomer pressure (P , monomer pressure; P^0 , monomer pressure at saturation); \circ , U-PVC; \bullet , S-PVC



Both the presence of chloromethyl branches^{7,32} and the two end groups **5** and **7**^{1,2,33,34} in PVC are the results of this mechanism. The normal fate of the expelled chlorine atom is to react with the monomer and thus bring about chain transfer to the monomer. When the monomer concentration is decreasing the probability of other reactions, e.g. according to scheme A, will increase. This is confirmed by the fact that HCl is evolved during polymerization after the pressure drop even when oxygen is absent³⁰. The increased formation of LCB at subsaturation polymerization³⁻⁶ is more evidence for the changes in the reaction pattern. Besides the above mentioned route to LCB the ordinary macroradicals must also be considered for the formation of radicals leading to LCB^{1,3,34}. An abstraction of hydrogen by a macroradical is likely to selectively occur from the chloromethylene groups:



An attack of macroradicals on the polymer chain will therefore not result in the formation of internal double bonds but in LCB with tertiary chlorine. The observed increased content of $\sim\text{CH}_2-\text{CH}_2\text{Cl}$ long chain ends in polymers with increased content of LCB^{1-3,34} is in accordance with mechanism C. However, according to our measurements up to $\frac{1}{3}$ of the LCB points contain tertiary hydrogen. This indicates that hydrogen, at least partly, is abstracted by chlorine atoms.

The two possibilities for radical **2** to react are very similar to the possible reaction for radical **4** in reaction scheme B. Radical **2** can propagate, forming a long chain branch (cf. the formation of chloromethyl branches). Alternatively, a chlorine atom can be expelled and an internal double bond is formed (cf. the formation of the 1-chloro-2-alkene end groups). The relation between propagation and chlorine repulsion for radical **4** is about 5:1 at saturated conditions and 55°C. With a decreasing monomer concentration this ratio will decrease which results in decreasing molecular weight⁶ and decreasing content of chloromethyl branches^{1,3}. The rate of formation of radical **2** should increase with increasing

monomer starvation. The increased formation of internal double bonds, free HCl and LCB with tertiary hydrogen can thus be explained by abstraction of methylene hydrogens by chlorine atoms according to mechanism A.

As mentioned earlier, internal allylic chlorine is considered to have a major influence on the thermal instability. The published data are, however, somewhat conflicting. Using KMnO_4 Braun and Quarg¹¹ obtained a linear relation between these two parameters with a non-zero rate at zero degrees of internal unsaturation. Lindenschmidt²² observed an unexpected behaviour, i.e. with increasing content of internal double bonds the stability increased. However, with regards to the shortcomings of the KMnO_4 method (see above) these results must be questioned. Abbäs and Sörvik²⁴ and Braun *et al.*²⁵ respectively have reported linear relations between the rate of dehydrochlorination and the content of internal double bonds using ozonolysis. In both cases extrapolation to zero degrees of unsaturation resulted in non-zero rates of dehydrochlorination. Burille¹⁶ has reported a similar result but the data points are rather scattered (correlation coefficient=0.63). However, a somewhat better correlation was obtained between the thermal stability and the total double bond content.

Minsker and his coworkers^{20,35} have also reported a linear relation between the rate of dehydrochlorination and internal unsaturation. In the first paper²⁰, this relation was obtained by ozonolysis and the actual labile structure was assumed to be β -chloroallylic ($\sim\text{CH}=\text{CH}-\text{CHCl}\sim$). The same number of cleavages was, however, also obtained by hydrolysis³⁵. Furthermore, the number of cleavages determined by hydrolysis was not changed after degradation whereas the ozonolysis value increased. As an explanation they proposed that the original internal unsaturation is of ketoallylic type ($\sim\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{CHCl}\sim$).

The formation of ketoallylic groups is suggested to occur by oxidation of allylic methylene groups during the polymerization and storage of PVC. Braun and Sonderhof³⁰ have carried out polymerizations of vinyl chloride in the presence of oxygen. The resulting polymers contained increased amounts of both internal double bonds and carbonyl groups. The content of the latter (up to 2.6/1000 VC) was several times higher than the content of internal unsaturation (up to 0.5/1000 VC). No bands at 1600 and 1675 cm^{-1} , which Minsker *et al.*³⁴ ascribed to ketoallylic groups, can be observed in the i.r. spectra of these polymers. Using FTi.r. Ahrens *et al.*³⁶ have shown that the intensity of a weak band at 1667 cm^{-1} can be directly correlated with the molecular weight and with the total content of double bonds determined by Wijn's method and they assigned it to 1-chloro-2-alkene end groups. The band at 1600 cm^{-1} has been assigned to moisture³⁷.

We have performed hydrolysis, according to Minsker, on three samples; sample A3 ($\text{C}=\text{C}_{\text{int}}=0.9/1000$ VC), sample C-7 ($\text{C}=\text{C}_{\text{int}}=0.25/1000$ VC) and a polymer obtained in the presence of oxygen, kindly supplied by Professor D. Braun and Dr D. Sonderhof, Deutsches Kunststoff Institut, BRD. As shown in Table 4, no change in the MWD could be observed.

As demonstrated earlier by ¹H n.m.r. the main unsaturated end group in PVC is $\sim\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$ ^{1,2}. If methylene groups adjacent to internal double bonds are as easily oxidized as suggested, the methylene group in this unsaturated end

Table 4 Molecular weight data from hydrolysis experiments

Sample No.	C=C _{int} ^a 1000 VC	Hydrolysis ^b	
		$\bar{M}_{n,0} \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$
A1	0.92	19.4	19.1
C-7	0.26	45.3	45.3
VC/O ₂ (copol.)	—	35.5	35.3

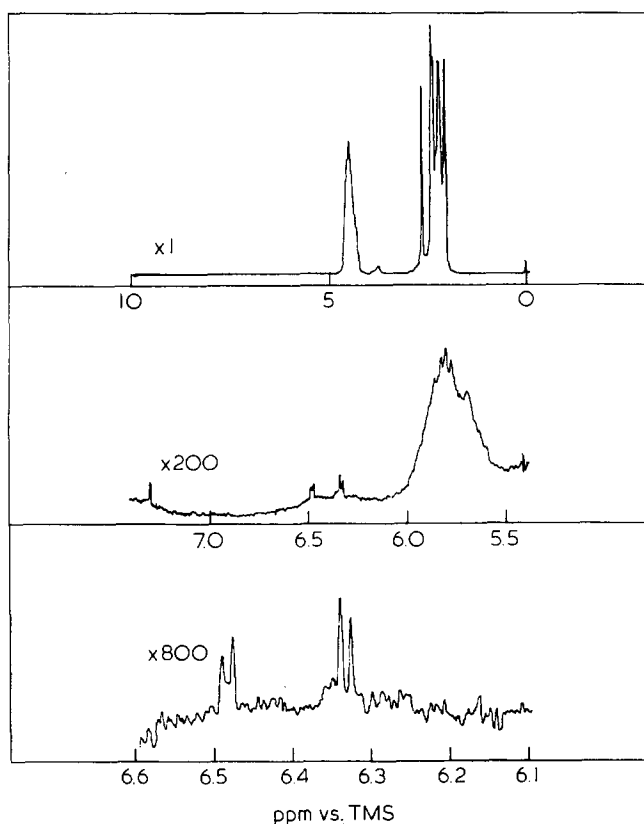
^a By ozonolysis^b $\bar{M}_{n,0}$, before and, \bar{M}_n , after treatment with KOH for 6 h at 25°C

Figure 5 200 MHz ¹H n.m.r. spectrum of sample A1. The spectrum was obtained with a 3% (w/v) solution in acetone-d₆/CS₂ (1:1) after 18000 scans. Double precision (32 bits wordlength) was used for accumulation and Fourier transformation was performed with floating point arithmetic

group should also be vulnerable to oxygen attack. We have investigated low molecular weight fractions from both the experimental and the commercial batch polymerized PVC qualities and have always observed that the 1-chloro-2-alkene structure accounts for the major part of the unsaturation. In 3-pentene-2-one the chemical shifts of the two ethylenic protons were found to be: =CH-C=O 5.99 ppm and CH₃-CH= 6.79 ppm. The following chemical shifts can then be predicted for a ketoallylic structure in PVC: -CHCl-CH¹=CH²-C(=O)-, δ_{H1} = 7.1 ppm and δ_{H2} = 6.5 ppm. In Figure 5 the 200 MHz ¹H n.m.r. spectrum of U-PVC A1 is given. This sample has the highest content of internal double bonds according to ozonolysis measurement; 1/1000 VC. There are some small peaks at 6.33, 6.5 and 7.28 ppm, however, these were found to be due to impurities in the solvent. The S/N ratio obtained in this experiment implies that the content of

ketoallylic groups should be less than 0.05/1000 VC. At present we do not consider that the polymers used in this investigation contain ketoallylic groups to any appreciable extent. Further studies with amongst other things ¹³C n.m.r. will, however, be performed.

With increasing content of internal double bonds the rate of dehydrochlorination is increasing in the U-PVC samples but the data points are rather scattered (see Figure 6). The S-PVC samples show a relation that is, at first sight, confusing; i.e. with increasing content the thermal stability is increased. The correlation for all samples between rate of dehydrochlorination and content of internal unsaturation is therefore rather poor (correlation coefficient = 0.88). However, comparisons of this kind are irrelevant as no other important factors are taken into account. The experiments with low molecular weight models have amongst other things showed that branch points with tertiary chlorine also have considerably lower stability than the ordinary structure¹⁵. The deleterious effect of tertiary chlorine has also been shown with copolymers of vinyl chloride and 2-chloropropene³⁸.

The influence of tertiary chlorine in ordinary PVC has, however, generally been neglected as the investigations made by Caraculacu and his coworkers^{39,40} with phenolysis have indicated that no tertiary chlorine is present. However, using ¹³C n.m.r. we have shown that the samples studied in this investigation do have butyl and long chain branch points with tertiary chlorine^{1,3} (see Table 5). In the U-PVC series the amounts of both tertiary and internal allylic chlorine increase with decreasing pressure. The relation between these two structures is about 5:1. Also the S-PVC fractions contain tertiary chlorine and the amount is decreasing when the number of internal double bonds is increasing. The relation between tertiary and internal allylic chlorine changes from about 20:1 to 1:1 for C-3 to C-7, respectively. The amount of internal double bonds in ordinary PVC is about 0.1–0.2/1000 VC (this paper)^{24,25} whereas the amount of tertiary chlorine is about 0.5–1/1000 VC^{1,3,34}.

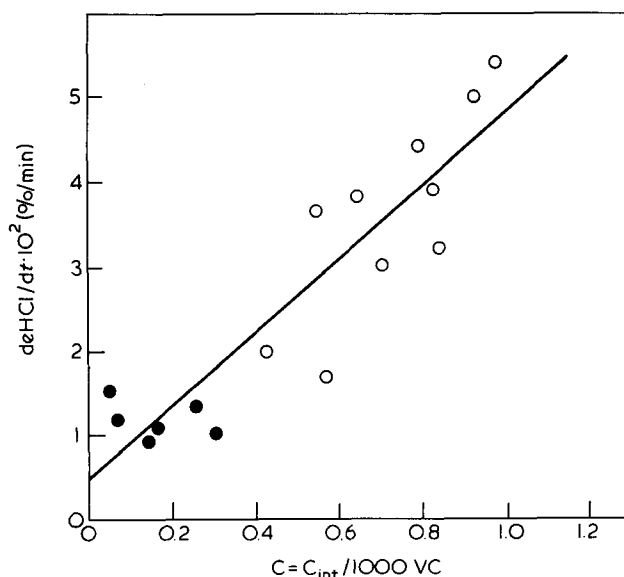


Figure 6 Relation between the rate of dehydrochlorination and the number of internal double bonds; ○, U-PVC; ●, S-PVC

Clearly, tertiary chlorine must contribute to the thermal instability of PVC. To determine the relative importance of tertiary and internal allylic chlorines both the respective amounts and reactivities must be taken into account. As mentioned earlier, internal allylic chlorine is generally considered to be the most labile structure. This is mainly based on degradations of model substances carried out by Asahina and Onozuka¹⁵. As shown in Table 6 widely differing data are, however, found at different conditions and we find it impossible to estimate a reactivity ratio between tertiary and internal allylic chlorine in the polymer from these data.

In our series of investigations we have measured the content of both tertiary chlorine³ and internal allylic chlorine. An estimation of the relative importance of these two structures is therefore possible. In our previous paper³ we made a direct comparison between the content of tertiary chlorine and the rate of dehydrochlorination. The data points for the S-PVC and the U-PVC follow the same linear relation with a correlation coefficient of 0.97. This relation is much better than that given for internal allylic chlorine. We therefore consider tertiary chlorine to be the most important labile structure not only in U-PVC but also in ordinary PVC.

We have tried to quantify the influence of the two labile structures by multiple regression analysis. The following mathematical model was used:

$$\text{deHCl} = k_T \text{Cl}_T + k_A \text{Cl}_A + B \quad (2)$$

where deHCl is the rate of dehydrochlorination at 190°C

Table 5 Content of tertiary chlorine in the U-PVC and S-PVC series^a

U-PVC		S-PVC	
Sample No.	Cl _T /1000VC ^b	Sample No.	Cl _T /1000VC ^b
A 1	5.4	C-3	1.0
A 2	4.8	C-4	0.8
A 3	4.8	C-5	0.7
A 4	3.2	C-6	0.7
A 5	4.0	C-7	0.9
A 6	3.7	C-8	0.5
A 7	4.2		
A 8	3.2		
A 9	1.9		
A10	2.1		

^a From ref. 3

^b Amount of tertiary chlorine (Cl_T) is approximated as the sum of the content of butyl branches and LCB (see text)

in nitrogen expressed in (%/min)·10⁻²; k_T and k_A are the rate constants of dehydrochlorination initiated by tertiary and internal allylic chlorine, respectively; the concentrations are expressed per 1000 VC. B includes the effects of end groups, eventual random dehydrochlorination and stabilizing effects of chloromethyl branches⁴² etc. The result of the data manipulation for three different sample sets are shown in Table 7. Clearly, the constants obtained for the U-PVC series and for all samples must be incorrect as k_A is negative.

The content of tertiary chlorine given in Table 5 was obtained as the sum of the contents of butyl and long chain branches³. All butyl branch points include tertiary chlorine. The relation between LCB points with hydrogen and chlorine was estimated to be 1:2 in sample A1 which was polymerized at 59% saturation pressure. It was much more difficult to measure this relation for samples with lower contents of long chain branches. In the S-PVC series it was even difficult to obtain an accurate separation between butyl and long chain branches. Therefore, the content of tertiary chlorine was approximated as the sum of the two branches. The obviously erroneous constants in Table 7 might be explained by this simplification. If it is assumed that 1/3 of the LCB points in all samples have tertiary hydrogen the data of the two series fit to equation (2) as follows:

$$\text{S-PVC; deHCl} = 1.05 \text{Cl}_T + 0.67 \text{Cl}_A + 0.30$$

correction coefficient = 0.92

$$\text{U-PVC; deHCl} = 0.91 \text{Cl}_T + 0.56 \text{Cl}_A + 0.15$$

correction coefficient = 0.87

As both k_T and k_A are positive the two relations are *per se* sensible. The assumption that a certain fraction of the LCB points in all samples contain hydrogen is therefore not ruled out. To prove it, ¹³C n.m.r. spectra of deuteride reduced PVC with low levels of LCB must be obtained with a considerably increased sensitivity.

The correlations obtained indicate that tertiary chlorine should have a somewhat higher reactivity than internal allylic chlorine. This is in accordance with the qualitative suggestion given above. However, before a more definitive statement of the relative importance of the two structures can be made, more data is needed. In the next paper in this series the results obtained with polymers prepared at different temperatures and relative monomer pressures will be reported.

Table 6 Comparison between the rate constant of dehydrochlorination for model compounds with tertiary and internal allylic chlorine

Tertiary chlorine		Allylic chlorine		Condition	$k_{p,A}/k_{p,T}$ ^a
Compound	Ref.	Compound	Ref.		
3-ethyl-3-chloropentane	15	4-chloro-2-hexene	15	10% solution in heptane	0.08
"	15	"	15	10% solution in heptane/ 2-chloro-propane (1:1)	0.04
"	15	"	15	10% solution in heptane/ 2-chloro-propane (1:9)	0.44
"	15	"	15	gas phase	0.89
"	15	"	15	liquid phase	4.8 · 10 ⁶
"	15	8-chloro-6-tridecene	41	"	11.5

^a $k_{p,A}$ dehydrochlorination rate constant for allylic chlorine model at 190°C

$k_{p,T}$ dehydrochlorination rate constant for tertiary chlorine model at 190°C

Table 7 Constants to equation (2) obtained by multiple regression analysis assuming that all LCB points have tertiary chlorine

Samples	k_T	k_A	B	Correction coefficient
S-PVC	1.11	0.28	0.30	0.84
U-PVC	1.11	-0.68	-0.02	0.95
All samples	0.96	-0.49	0.50	0.98

CONCLUSIONS

In the polymerization of vinyl chloride, internal unsaturated groups are formed as a result of an attack of chlorine atoms on the methylene group in the polymer chain. With increasing monomer starvation at subsaturation polymerizations this reaction increases compared with the reaction with monomer in the chain transfer step. In conventional PVC the content of internal double bonds is about 0.1–0.2/1000 VC. No evidence of conjugation between C=C double bonds and carbonyl groups was found. The internal chloroallylic groups contribute to the thermal instability of PVC. However, butyl and long chain branch points containing tertiary chlorine are more frequent in number, the content being about 0.5–1/1000 VC, and they are more important for the instability.

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