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Formation of Anomalous Structures in PVC and Their Influence on Thermal Stability.
I. Endgroup Structures and Labile Chlorine Substituted by Phenol

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ABSTRACT

The thermal stability and structural details were compared for fractions of S-PVC and a series of "U-PVC" prepared at subsaturation conditions. Molecular weights and long chain branching were obtained by GPC and viscometry. "Labile chlorine" was determined by phenolysis, double bonds by bromination, and endgroup structure by NMR. The rate of thermal dehydrochlorination was determined in nitrogen at 190°C. In S-PVC there are few tertiary chlorine, and phenolysis therefore measures allylic chlorine. By NMR it was found that $\sim\!\sim CH_2{-}CH{=}CH{-}CH_2Cl$ is the main unsaturated structure. Phenolysis and bromination therefore mainly give a measure of this group. The main saturated chain end is $\sim\!\sim CHCl{-}CH_2Cl$. These groups account for 80% of the endgoups and are the result of the mechanism of chain transfer to monomer: head-to-head addition followed by 1,2-Cl migration and Cl· elimination. They have only a weak influence on the thermal stability, however. U-PVC, on the other hand, shows a strong relation between phenolysis and thermal stability. By NMR it was shown that the relative content of 1-chloro-2-olefin structures is considerably lower than in S-PVC although the total unsaturation and the relative amount of 1,2-dichloro ends are similar. 1,3-Dichloro ends were also found. The observed structural differences cannot possibly account for the lower thermal stability of U-PVC. They are, however, an indication of changes in the reaction pattern due to the monomer starvation. Apparently, other, more labile structures are also formed at subsaturation conditions.

INTRODUCTION

Anomalous structures have long been considered to be the main reason to the thermal instability of PVC. The actual nature of these structures is still disputed, however. In the first place, the discussion is concentrated to labile carbon-chlorine bonds, "labile chlorine" (Cl_L) and especially "allylic chlorine" (Cl_A) and "tertiary chlorine" (Cl_T). The very low content of nonregular structures in ordinary PVC and the difficulty to determine their specific influence have so far hindered further elucidation.

A well-known hypothesis is that polymer with reduced stability is formed at the end of conventional polymerizations, i.e., after the pressure drop. As previously reported, we have used polymerization at subsaturation conditions as a model for these stages of the process [1-3]. We found that even a fairly low degree of monomer starvation gives polymer with inferior thermal stability. The amount of low molecular weight species and long-chain branching (LCB) both increased. By combination of the data it was indicated that endgroups rather than long-chain branch points are related to the decreased thermal stability of subsaturation PVC (U-PVC).

In a series of investigations we have now determined different irregular structures in PVC and evaluated their effect on the thermal stability. We have compared U-PVC with fractions of ordinary suspension PVC (S-PVC) with the same range of molecular weight. In this paper we report the results of determinations of Cl_L by phenolysis, double bonds by bromination, and endgroup structure by ^{1}H-NMR and ^{13}C-NMR.

EXPERIMENTAL

Materials

By polymerization of VC at subsaturation pressure as described elsewhere [3], a series of materials with different molecular weight and LCB was obtained (Series A, Table 1). The polymerization

TABLE 1. Series A, U-PVC

Sample	P/P_0	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$\frac{\text{LCB}}{\text{1000 VC}}$	$\frac{\text{deHCl}}{\text{dt}} \times 10^2$ %/min
A1	0.59	13.7	50	2.8	5.47
A2	0.59	17.3	72	3.1	4.42
A3	0.67	17.6	62	2.7	5.05
A4	0.67	20.0	75	1.7	3.85
A5	0.67	20.7	70	2.0	3.95
A6	0.75	21.5	98	3.2	3.80
A7	0.75	23.4	95	2.1	3.25
A8	0.85	25.8	89	3.4	3.03
A9	0.85	35.9	113	0.9	1.70
A10	0.92	40.7	137	1.1	2.00

temperature was 55°C and the monomer pressure was varied between 59-92% of the saturation pressure of VC at 55°C.

In order to compare U-PVC with ordinary PVC we have also investigated a commercial S-PVC polymerized at the same temperature, Pevikon S-687, KemaNord AB, Sweden. This polymer was fractionated by extraction to give samples within the same range of molecular weight as the U-PVC series. Fractionating conditions and sample data are given in Table 2. As the original planning was extended, it was necessary to prepare two series of materials, Series B and C.

Phenolysis

As a measure of Cl_L we have chosen to determine the amount of chlorine which can be substituted by phenol according to Caraculacu et al. [4]. 0.5 g of the sample was heated for 96 h at 60°C in 20 g phenol (p.a.). After cooling, excess phenol was removed by decantation with 2×100 mL methanol (p.a.) at 5°C. The material was then dissolved in 20 mL tetrahydrofurane (THF) free of peroxide. The solution was precipitated in 100 mL methanol at 5°C. The purification with THF-methanol was repeated 3 times. The sample was then dried for 24 h at 40°C in vacuum. The degree of substitution was determined by NMR (see below).

TABLE 2. Series B and C, S-PVC

Sample	Extracted from	Extraction system[a]	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$\frac{LCB}{1000\ VC}$	$\frac{deHCl}{dt} \times 10^2$ %/min
B1	B7	Acetone/hexane (1.4:1)	19.8	42	1.8	1.46
B2	B7	Acetone/methanol (7.3:1)	23.4	46	1.0	1.20
B3	B7	1,2-Dichloroethane/methanol (7.7:1)	24.5	51	0.4	1.22
B4	B7	Acetone	29.1	57	0.1	0.95
B5	B2 residue	Acetone	42.3	75	0.1	0.86
B6	B1 residue	Acetone	38.2	72	0.2	0.83
B7	-	-	45.3	100	0.3	1.0
B8	B6 residue	Complete dissolution	58.6	111	0.2	0.9
C1	C7	Acetone/hexane (1:3)				
C2	C7	Acetone/ethanol (3:1)	9.2	17.3	1.5	
C3	C7	Acetone	19.3	40	1.0	
C4	C7	Acetone/THF (95:5)	21.0	43.5	0.6	
C5	C7	Acetone/THF (90:10)	26.8	54	0.6	
C6	C7	Acetone/THF (83:17)	33.4	69	0.4	
C7	-	-	46.3	102	0.3	
C8	C4 residue	Complete dissolution	60.1	113	0.3	

[a] Series A, Soxhlet extraction; Series B, extraction at 25°C.

Bromination

The total amount of double bonds was determined by bromination in solution according to Morikawa [5]. 0.25 g PVC was dissolved for 3 h at 60°C in 20 mL dichloroethane (EDC) in a 25-mL measuring flask. To this solution were added 1 mL 0.1 M mercury acetate solution in dry acetic acid, 2 mL bromine solution (0.04 g/L EDC), and EDC to the mark. The flask was then kept in darkness for 24 h. The dry acetic acid was prepared by refluxing concentrated acetic acid and acetic anhydride (4:1) for 3 h.

The solution in the measuring flask was poured under agitation into a vessel with 30 mL 10% (w/v) KI (aq) and the flask was rinsed with 5 mL EDC. The liberated iodine was titrated potentiometrically [6] with 0.0125 M thiosulfate solution. A blank without PVC was treated in the same way. The content of double bonds per 1000 VC units was calculated by

$$\mathrm{C{=}C/1000\ VC} = \frac{(B - V)}{2m}\,\underline{M}\,62{,}500 \times 10^{-3}$$

where B = mL thiosulfate in blank titration
V = mL thiosulfate in sample titration
m = sample weight in mg
M = concentration of the thiosulfate solution, mol/L

Molecular Weights and LCB

Gel chromatography (GPC) and viscometry were used for determination of molecular weight distribution (MWD) and LCB. Details of the GPC analysis and viscometry measurement have been given earlier [7]. Intrinsic viscosity was determined by dilution in THF 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 THF as solvent was used. The column combination consisted of five Styragel columns with permeabilities ranging from 10^3 to 10^7 Å, giving good separation in the molecular weight range of interest. To calculate MWD, MW averages, and LCB from GPC and intrinsic viscosity, the computer program devised by Drott and Mendelson [8] was used, assuming trifunctional branch points. The calibration for linear PVC was obtained via the universal calibration curve as described earlier [7].

NMR Measurements

^{1}H-NMR at 270 MHz (Bruker WH 270) or 200 MHz (Varian XL 200) was used for the determination of incorporated phenol and for the

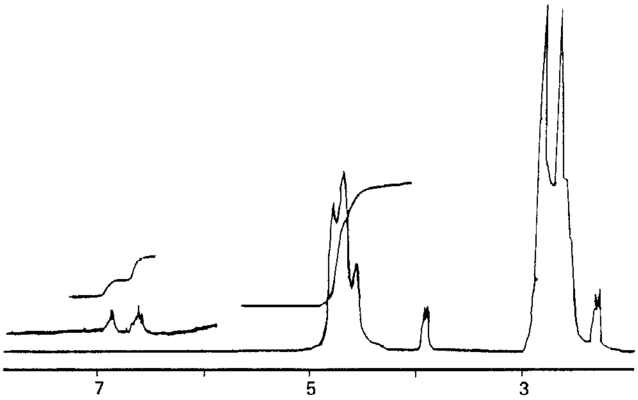


FIG. 1. ^{1}H-NMR spectrum (270 MHz) of phenolyzed sample B2, 5% in THF-d_8, 850 scans. Chemical shifts with reference to TMS.

study of endgroups. ^{13}C-NMR at 50.3 MHz (Varian XL 200) was also used for endgroup studies. 5% solutions of the phenolyzed samples were prepared with either THF-d_8 or acetone-d_6/CS_2 (1:1) as solvent. 800-1000 scans were accumulated before Fourier transformation. An example of the NMR spectrum at 270 MHz is given in Fig. 1. The magnified signal downfield in the spectrum shows the aromatic protons of reacted phenol. In the case of incomplete purification a signal at about 7.5 ppm from the para proton of unreacted phenol appears. The amount of phenol groups and, accordingly, the concentration of Cl_L were calculated from the area of the aromatic signal relative to the area of the CHCl-signal.

^{1}H-NMR analysis of endgroup structures was performed in 5% solutions in $CDCl_3$ at 200 and 270 MHz. About 300 scans were accumulated. The ^{13}C-NMR spectra were obtained with 20-30% solutions in $CDCl_3$. The flip angle was 60° and the accumulation time was 1 s. About 100,000 scans were accumulated.

Thermal Stability

Thermal stability was measured by dehydrochlorination. Experimental details have been given earlier [9]. Bulk samples were treated at 190°C in pure nitrogen atmosphere and HCl was measured by conductometry. The rate of dehydrochlorination is expressed as evolved HCl (in percent of the theoretical amount) per minute. The linear part of the conversion curve between 0.1 and 0.3% was used. Results are given in Tables 1 and 2.

RESULTS AND DISCUSSION

Analysis by Chemical Methods

It is generally assumed that the same types of chemical bonds, i.e., the same Cl_L, are responsible for the reactivity whether the polymer is affected by thermal energy or chemical agents. It has therefore been considered that substitution reactions are a convenient way to determine Cl_L. Reactions with cadmium acetate [10, 11] and with triethylaluminum [12] have been used but the results have been disputed.

In a series of papers, Caraculacu and co-workers have described a method based on substitution of Cl_L with phenol. IR [13] and later UV [4] spectroscopy were used for determination of incorporated phenol. The published data indicate a detection limit of 2 and 0.5 Cl_L/1000 VC, respectively.

In this work we have used phenolysis as a method for determining Cl_L. The degree of substitution was determined by NMR, however, which extended the detection limit to $\leq$0.2/1000 VC.

The results of the phenolysis on U-PVC and S-PVC fractions, Series A and B, respectively, are given in Table 3. For U-PVC there is a strong relation between $(Cl_L)_{phenol}$ and the rate of dehydrochlorination (Fig. 2). For S-PVC the relation is much weaker. Obviously different types of Cl_L are operative in the two series of materials. $(Cl_L)_{phenol}$ can thus not be used as a generally valid measure of the tendency to dehydrochlorination.

Using both low molecular weight [14] and high molecular weight [4, 15] model substances, Caraculacu et al. have shown that Cl_A and Cl_T but not secondary chlorine are substituted by phenol. In their first measurements on ordinary PVC, Caraculacu et al. [13] used IR to determine incorporated phenol. As no phenol was detected, the conclusion was that no Cl_T exists in PVC. Later [4], UV was used as a more sensitive detector and a content of 1-1.5 Cl_L/1000 VC was found. It was concluded that almost all Cl_L were Cl_A as the content of Cl_L decreased with increasing molecular weight.

Naturally, if present, Cl_T is positioned at branch points. The short chain branch structure has been investigated with IR and recently with ^{13}C-NMR on reduced PVC. Using $LiAlD_4$ and ^{13}C-NMR, Bovey et al. [16] found that the short chain branches in ordinary PVC consist of chloromethyl groups and that hydrogen and not chlorine is attached to the tertiary carbon. This was confirmed by Starnes et al. [17] who investigated commercial and experimental PVC samples

TABLE 3. Phenolysis and Bromination Data

Sample	$\frac{Cl_L}{1000\ VC}$	Sample	$\frac{C{=}C}{1000\ VC}$
A1	3.44	A1	4.14
A2	2.98	A2	3.62
A3	3.18	A3	3.92
A4	2.48	A4	2.94
A5	2.20	A5	2.78
A6	1.96	A6	2.74
A7	1.62	A7	2.62
A8	1.62	A8	2.44
A9	0.84	A9	1.64
A10	0.98	A10	1.62
B1	2.16	C2	6.46
B2	1.64	C3	3.10
B3	1.62	C4	3.18
B4	1.32	C5	2.20
B5	0.84	C6	1.88
B6	0.82	C7	1.40
B7	0.66	C8	1.22
B8	0.60		

polymerized in the temperature range 43-75°C. In a PVC sample prepared at 100°C they also found 2-chloroethyl groups with Cl_T at the branch point [18]. In the spectra of ordinary PVC so far published from these investigations, no chloroethyl groups can be detected. Consequently, any eventual Cl_T in conventional PVC should be found at the long chain branch points. By comparing viscometric data for reduced PVC and linear polyethylene [19], the amount of LCB was estimated to be less than 1 per macromolecule. An estimation based on the value of M_w/M_n gave less than 0.2/1000 VC [20]. Measurements based on GPC and viscometry on PVC [7] and also with ^{13}C-NMR on reduced PVC [17] have given 0-1 LCB per 1000 VC. In the present investigation the amount of LCB was in the order of 0.1-1.8/1000 VC in the S-PVC fractions and 0.9-3.5/1000 VC in the U-PVC samples (Tables 1 and 2).

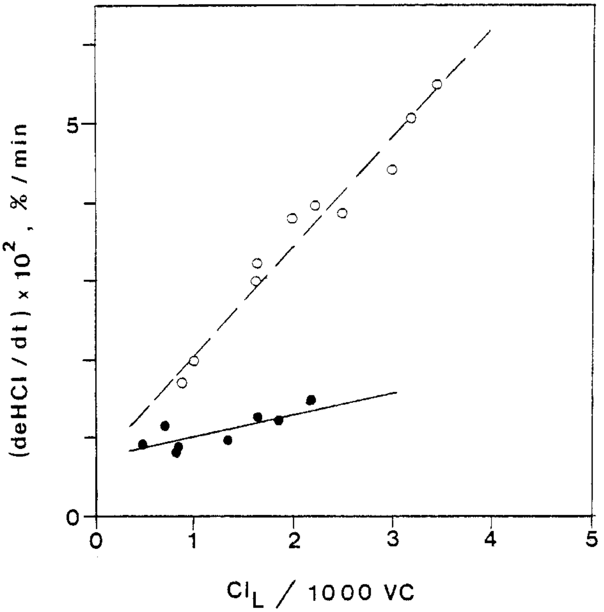


FIG. 2. Relation between rate of dehydrochlorination and amount of labile chlorine determined by phenolysis: (○) U-PVC, Series A; (●) S-PVC, Series B.

Our measurements show that for both S-PVC and U-PVC, Cl_L increases with decreasing molecular weight. Cl_L therefore seems to be related to the amount of chain ends. The LCB in the S-PVC samples is low and it is difficult to observe its eventual influence on Cl_L. In the U-PVC, however, LCB is higher and increases with decreasing molecular weight. At least in the U-PVC, Cl_L could therefore equally well be related to chain ends as branch points. In an attempt to use the phenolysis data to discriminate between Cl_A and Cl_T, we have recalculated the Cl_L values in Table 3. From Fig. 3 it is obvious that Cl_L given per chain end is independent of LCB. As a first approximation the fraction of chain ends with Cl_A is assumed to be constant. The results therefore indicate that Cl_L, as determined, consists of Cl_A and that no Cl_T is present in the long chain branch points. From their NMR measurements on a deuterated sample of PVC polymerized at 100°C, Starnes et al. [18] concluded that all long chain branch

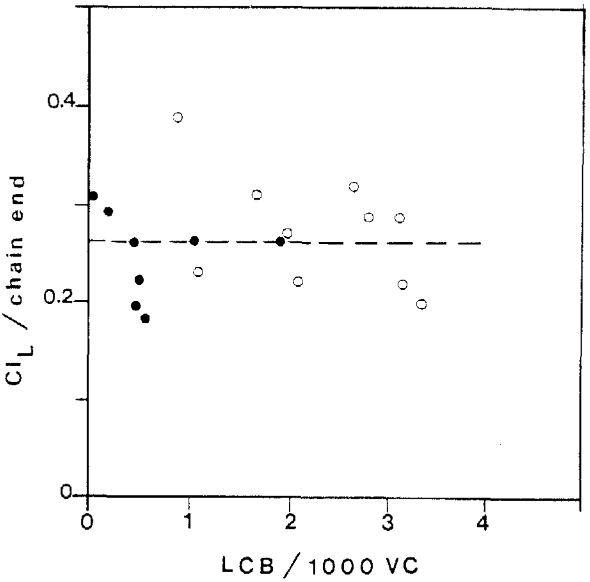


FIG. 3. Relation between labile chlorine per chain end and degree of long chain branching; (○) U-PVC, Series A; (●) S-PVC, Series B.

points in that material contain Cl_T. In our laboratory similar measurements on the reduced and deuterated S-PVC and U-PVC samples are now in progress.

The presence of double bonds is, of course, the prerequisite for Cl_A. The strong tendency to chain transfer to monomer in VC polymerization should lead to about 0.8-0.9 unsaturated chain ends per macromolecule. For a polymer with M_n = 50,000, i.e., within the normal commercial range, this means about one per 1000 monomer units, which is comparable to the amount of Cl_L found. As the amount of internal unsaturation is one order of magnitude lower [21], it is reasonable to believe that Cl_A could mainly be found in chain ends.

The result of the determinations of the total content of double bonds is given in Table 3. The value for the unfractionated S-PVC (Sample C7) is approximately the same as that found by Boissel [6] for a comparable polymer. In Fig. 4 the number of double bonds is plotted against the reverse of $\overline{M}_n$ for both the S-PVC and U-PVC samples. A straight line which can be extrapolated to the origin is obtained, in good agreement with the above-mentioned assumptions. The slope of the line points to about 1 double bond per macromolecule.

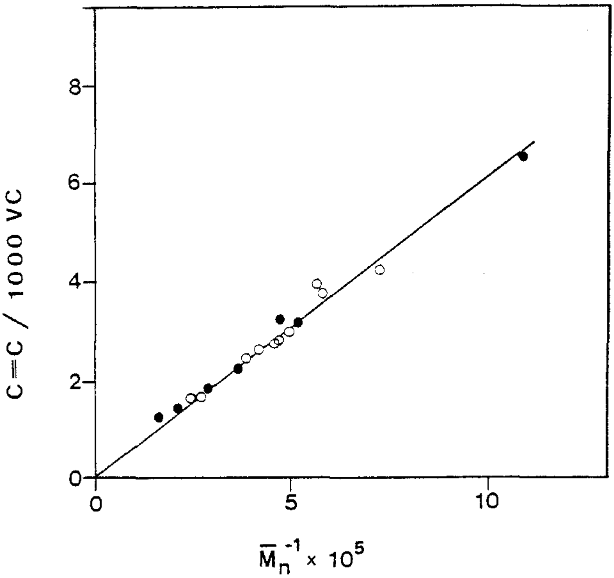


FIG. 4. Relation between amount of double bonds and $1/\overline{M}_n$: (○) U-PVC, Series A; (●) S-PVC, Series C.

For the series of U-PVC both bromination and phenolysis were performed on the same materials and a direct correlation is possible. For fractions of S-PVC, lack of material forced us to perform the reactions on two series, phenolysis with Series B and bromination with Series C. As the Cl_L content also gives a straight line when plotted against the reverse of $\overline{M}_n$, Fig. 5, a comparison between phenolysis and bromination could also be carried out for the S-PVC series. In Fig. 6 the straight line refers to the S-PVC. The circles representing the U-PVC samples fall along this line. Obviously, these chemical methods cannot differentiate between the two types of materials in spite of their great difference in thermal stability.

The slope of the line is 1, which implies that every double bond results in a Cl_A. The extrapolation does not go through the origin. Accordingly, a "rest content" around 0.8 double bonds per 1000 VC should not be related to Cl_A. So far, we have no explanation to this. Polyene sequences or underestimation of phenol-substitution would, of course, only influence the slope and not the intercept in the correlation between Cl_A and double bonds. One possible reason could have been that bromination, beside addition, also leads to substitution.

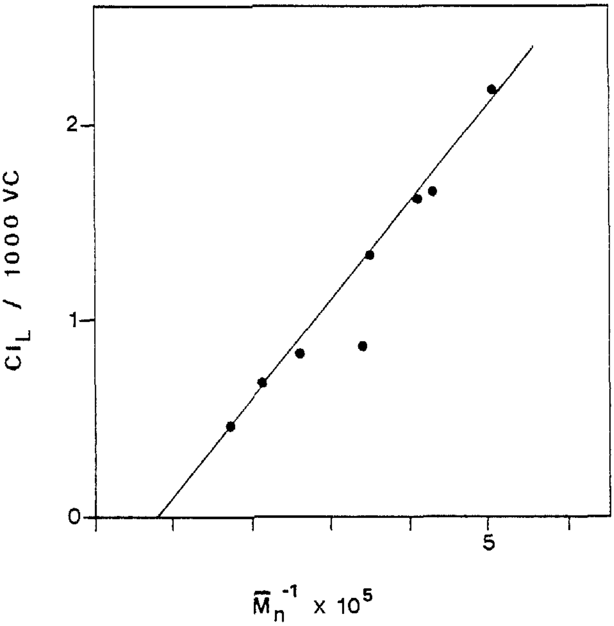


FIG. 5. Relation between amount of labile chlorine and $1/\bar{M}_n$ for S-PVC, Series B.

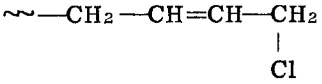
A substitution reaction would be independent of double bond content but influenced by the PVC and bromine concentrations. However, brominations with different concentrations of PVC did not indicate any substitution.

Accordingly, our results from bromination and phenolysis indicate:

all "labile chlorines" are allylic; long-chain branch points do not contain tertiary chlorine.
double bonds are mainly situated at chain ends.
unsaturated structures mainly include allylic chlorine.
the large difference between S-PVC and U-PVC in thermal stability is not revealed.

NMR Measurements

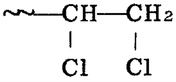
In order to elucidate the structure of the unsaturated chain ends, we have investigated the S-PVC samples with ^{1}H-NMR and ^{13}C-NMR. As further discussed below, we found the main unsaturated chain end structure to be



$\sim\!\!-CH_2-CH=CH-\underset{\substack{|\\ Cl}}{CH_2}$

I

Similarly, for the saturated chain end structure:



$\sim\!\!-\underset{\substack{|\\ Cl}}{CH}-\underset{\substack{|\\ Cl}}{CH_2}$

II

In order to get strong signals of end structures, we first studied the fraction with the lowest molecular weight (C1). The proton spectrum of this fraction is given in Fig. 7. The larger peaks originate from the $C\underline{H}_2$ and $C\underline{H}Cl$ protons in the chain. The smaller peaks indicated are magnified in Figs. 8-10. Protons bonded to unsaturated carbons show a multiplet at the expected position 5.5-5.9 ppm (Fig. 8). Upfield in relation to the main $C\underline{H}Cl$ peak there are some signals which have about the same intensity: a well-resolved doublet around

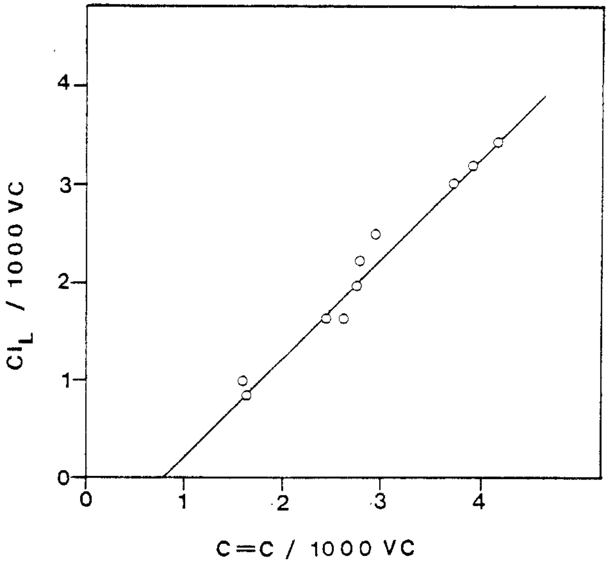


FIG. 6. Relation between amount of labile chlorine and amount of double bonds: (o) U-PVC, Series A; (—) S-PVC, Series B and C.

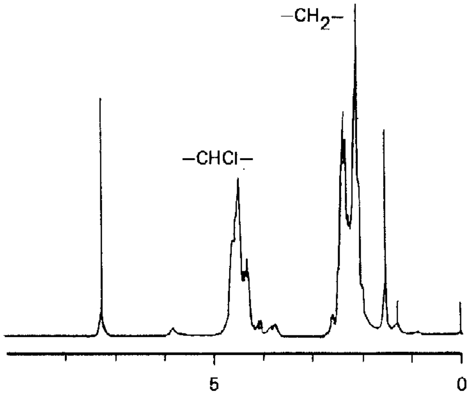


FIG. 7. ^{1}H-NMR spectrum (200 MHz) of a low molecular weight S-PVC fraction (Sample C1), 5% in CDCl$_3$, 300 scans.

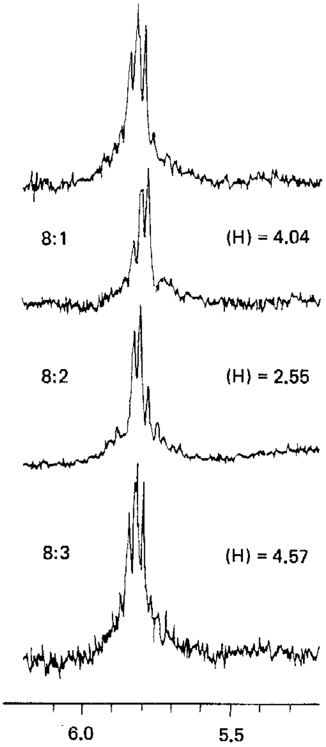


FIG. 8. Part of the proton spectrum in Fig. 7 showing olefinic protons. 8:1-8:3 show the effect of decoupling at given frequencies, (H), in ppm.

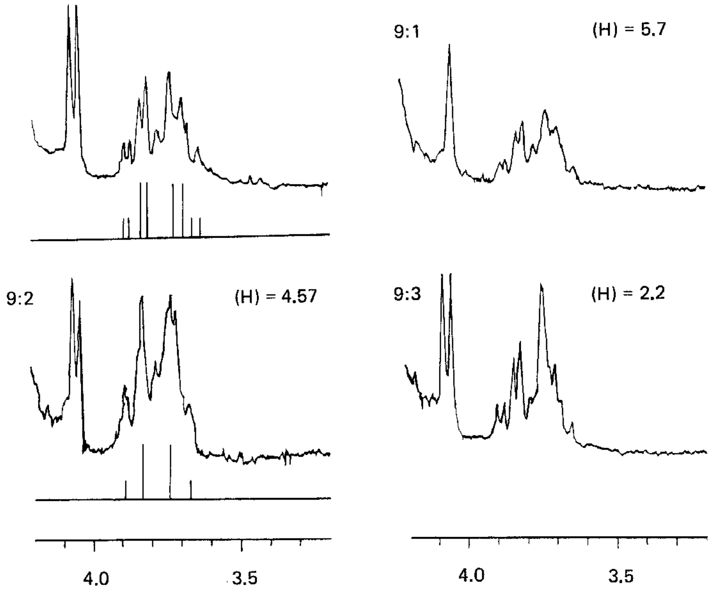
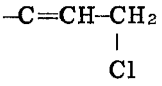
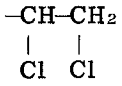


FIG. 9. Part of the proton spectrum in Fig. 7, showing CH_2Cl groups. 9:1-9:3 show the effect of decoupling at given frequencies, (H), in ppm.

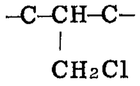
4.05 ppm and a more complex pattern between 3.6 and 3.9 ppm (Fig. 9). The chemical shift indicates that they are CH_2Cl groups. The following structures can per se be associated with the doublet:


$-C{=}CH-\underset{Cl}{\underset{|}{CH_2}}$

I_1


$-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$

II


$-C-\underset{CH_2Cl}{\underset{|}{CH}}-C-$

III

In a separate investigation with ^{13}C-NMR it was found that the content of Structure III, i.e., the short-chain branching, was constant (4-4.5/1000 VC) irrespective of the molecular weight [22]. Contrary to that, the relative area of the doublet compared to the main peaks was found to increase linearly with $1/\overline{M}_n$. The slope corresponds to 0.7 such groups per macromolecule [23]. The doublet at 4.05 ppm must therefore be associated with one of the chain end Structures I_1 or II.

To discriminate between these two possibilities, decoupling experiments were performed. Irradiating at 4.05 ppm gives a simpler pattern in the unsaturated region (Fig. 8). If the irradiating frequency is set to 5.7 ppm, the doublet at 4.05 turns to a singlet (Fig. 9:1). Decoupling with frequencies corresponding to the main CHCl peak does not influence the doublet, but results in a simpler pattern between 3.6 and 3.9 ppm. These observations show unambiguously that the doublet can be assigned to Structure I_1.

In Structure II the CHCl carbon is chiral which should result in an ABX spectrum. The AB part (CH_2Cl–) is positioned between 3.6 and 3.9 ppm as shown in Fig. 9. Decoupling at frequencies corresponding to the main CHCl peak gives the AB spectrum of $-CH_2Cl$ (Fig. 9:2). The geminal coupling constant is J_{HCH} = 11 Hz, and the two different vicinal constants are $J_{HCCH,1}$ = 4.5 Hz and $J_{HCCH,2}$ = 8 Hz. These values are in good agreement with those reported for 1,2-dichloropropane J_{HCH} = 11.1 Hz, $J_{HCCH,1}$ = 4.65 Hz, and $J_{HCCH,2}$ = 9.05 Hz [24].

Beside the peaks originating from $-CHCl-CH_2Cl$ chain ends, there are also peaks from chloromethyl branching and possibly $-CH_2-CH_2Cl$ chain ends around 3.75 ppm (see spectra Fig. 9:3), where decoupling frequency is at the main CH_2 protons (2.2 ppm). If the amount of chloromethyl branching is considered, chain ends according to Structure II would then account for about 90% of the saturated chain ends in the S-PVC fraction. The other saturated chain ends should be CH_2-CH_2Cl ends. By ^{13}C-NMR on deuterated PVC it has also been shown that the major part of the saturated chain ends consists of Structure II and that the rest is $-CH_2-CH_2Cl$ [18].

A third area of interest in the spectrum is around 2.5 ppm where a triplet is found (Fig. 10). Reasonably, this triplet should originate from CH_2 protons which are shifted downfield by a neighboring double bond. Irradiating at this frequency change the multiplet of the olefinic protons to a simpler pattern, while irradiating at $-CHCl$ protons does not have any influence (Figs. 8:2 and 8:3). The previously given Structure I is in accordance with these observations. The appearance of a triplet instead of two neighboring doublets at 2.5 ppm is due to equality of the coupling constants. They are both about 7 Hz.

A comparison of the area of the doublet at 4.05 ppm and the multiplet at 5.6-5.9 ppm (assuming $-CH{=}CH$ structures) indicates that Structure I accounts for 80% of the unsaturation in this sample. Complementary measurements on fraction C1 were performed with ^{13}C-NMR (Fig. 11). A small peak at 130 ppm can be assigned to unsaturated carbons. This area of the spectrum is magnified in Trace b, which also reveals other, smaller peaks. The fast pulsing gives a rather poor accuracy in a quantitative evaluation, but the larger peak seems to account for 80% of the unsaturation. The ^{13}C-NMR measurements therefore confirm that other unsaturated structures besides Structure I are present in lower extent.

In their work with model substances for unsaturated chain end structures in PVC, Bezdadea et al. [25] considered Structure I

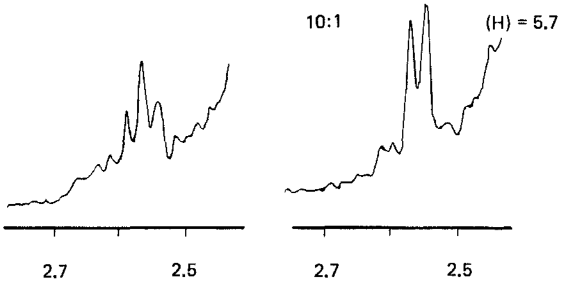


FIG. 10. Part of the proton spectrum in Fig. 7 showing CH_2 protons in Structure I. 10:1 shows the effect of decoupling at olefinic protons.

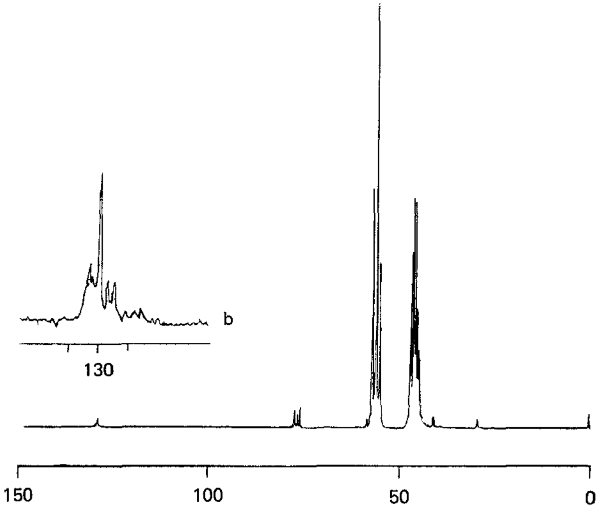
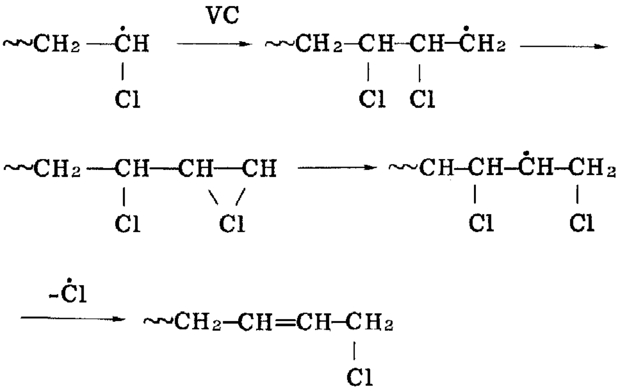


FIG. 11. ^{13}C-NMR spectrum (50.3 MHz) of a low molecular weight S-PVC fraction (Sample C1), 25% in $CDCl_3$, 100,000 scans.

as possible and suggested the following mechanism for its formation:



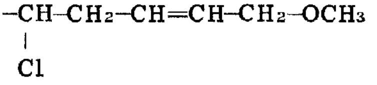
$$\sim\sim CH_2-\underset{\text{Cl}}{\dot{C}H} \xrightarrow{VC} \sim\sim CH_2-\underset{\text{Cl}}{CH}-\underset{\text{Cl}}{CH}-\dot{C}H_2 \longrightarrow$$

$$\sim\sim CH_2-\underset{\text{Cl}}{CH}-CH-CH \ (\text{bridging Cl}) \longrightarrow \sim\sim CH-\underset{\text{Cl}}{CH}-\dot{C}H-\underset{\text{Cl}}{CH_2}$$

$$\xrightarrow{-\dot{C}l} \sim\sim CH_2-CH=CH-\underset{\text{Cl}}{CH_2}$$

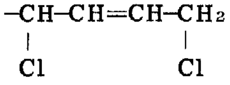
Their ^{1}H-NMR measurements (100 MHz) on the model substance, 1-chloropentene-2, showed the doublet at 3.95 ppm. We found a slightly different value, 4.01 ppm, on a sample sent to us from this group [26]. Caraculacu and Bezdadea [27] then extended their NMR studies to ordinary unfractionated PVC samples. They did not find Structure I but reported some other unsaturated chain end structures. Working with ether-soluble fractions of extremely low molecular weight (DP = 10-12), Pétiaud and Pham [28] showed Structure I to be the main unsaturated structure. They also argued that this structure is present in ordinary unfractionated PVC. As an alternative to the previously mentioned mechanism, they also suggested one based on accidental dehydrochlorination of head-to-tail additions.

Recently, Schwenk et al. [29] presented proton and carbon spectra of a low molecular weight fraction ($\overline{M}_n \sim 1500$) obtained by Soxhlet extraction of mass PVC with methanol. They found the following unsaturated structures:



$$-\underset{\text{Cl}}{CH}-CH_2-CH=CH-CH_2-OCH_3$$

IV

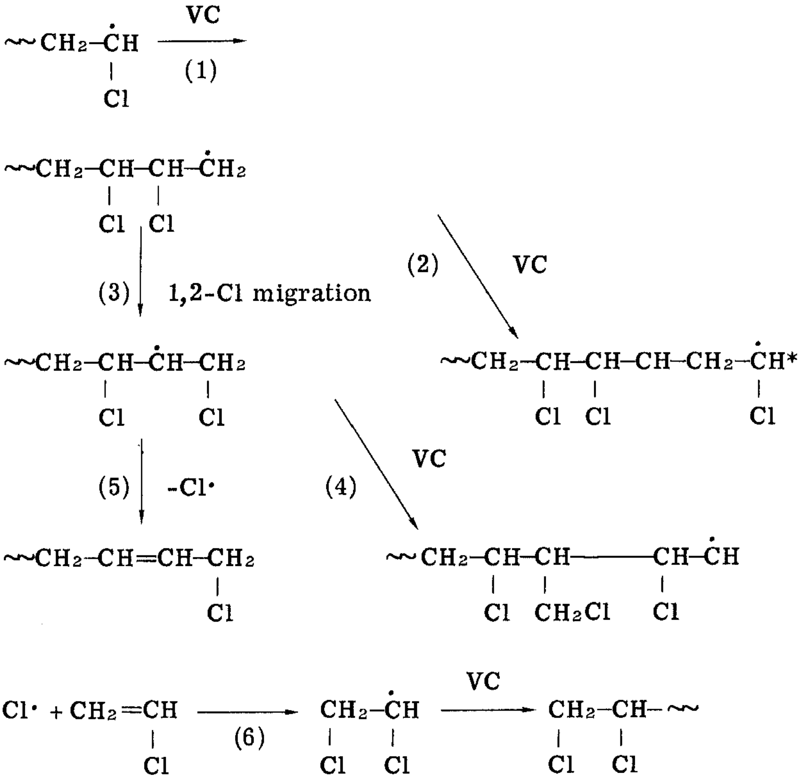


$$-\underset{\text{Cl}}{CH}-CH=CH-\underset{\text{Cl}}{CH_2}$$

V

IV is said to be a result of methanolysis of Structure I. The CH_3-O protons are seen as a sharp singlet at 3.35 ppm. As in our spectra, a doublet is observed at 4.05 ppm. This doublet is assigned to the $-CH_2O$ protons, however. Referring to Bezdadea et al. [25], the $C\underline{H_2}Cl-C=C$ protons are said to give a doublet at 3.9 ppm. As discussed above, we have found a value of 4.05 for the latter protons. In our case this doublet cannot originate from methanolyzed I (methanol only used cold as precipitant). This is confirmed by the absence of a singlet at 3.35 ppm.

The presence of chloromethyl branches and the fact that the unsaturated and saturated end groups mainly consist of Structures I and II, respectively, is in acoordance with the following reaction scheme:



The head-to-head addition followed by 1,2-Cl migration was originally proposed by Rigo et al. [30] for the formation of short-chain branches. Recently, this mechanism was proven by Starnes et al. [31] to favor the alternative route via 1,2-H migration from an ordinary macroradical [29, 32]. As previously mentioned, Bezdadea et al. [25] considered Reactions (1), (3), and (5) as likely for the formation of Structure I. For an ordinary PVC with $\overline{M}_n$ = 50,000, the the observed data indicate that 6 per 1000 head-to-head additions result in short-chain branching [17] and 1 in chain transfer. With reference to the distribution of endgroups given above, it can be further concluded that on the average four out of five chains are

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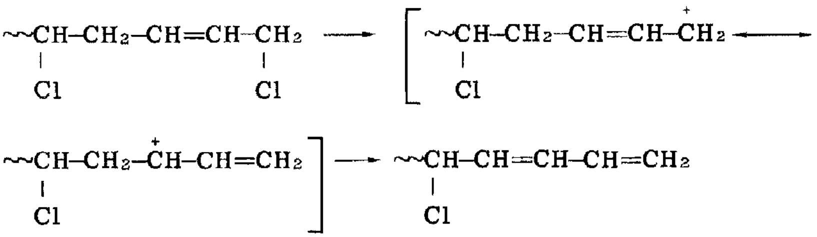
*Reaction is not likely as no internal head-to-head structure has been detected, e.g., by ^{13}C-NMR [31].

started by chain transfer, in good agreement with kinetic measurements [33].

Comparison between Stability Measurements and Structural Determinations

By chemical methods it was found that the double bonds mainly are situated at the chain ends and that they mainly include allylic chlorine. This is in good agreement with the NMR measurements which showed that Structure I is the main unsaturated structure in the S-PVC samples. The chemical methods also indicated that there are few, if any, Cl_T.

The allylic chlorine in Structure I is isolated, but it is likely that a diene structure can form via an ionic mechanism:



$$\sim\underset{\displaystyle Cl}{CH}-CH_2-CH=CH-\underset{\displaystyle Cl}{CH_2} \longrightarrow \left[\sim\underset{\displaystyle Cl}{CH}-CH_2-CH=CH-\overset{+}{C}H_2 \longleftrightarrow \sim\underset{\displaystyle Cl}{CH}-CH_2-\overset{+}{C}H-CH=CH_2\right] \longrightarrow \sim\underset{\displaystyle Cl}{CH}-CH=CH-CH=CH_2$$

This will lead to an allylic chlorine which can initiate a polyene sequence in thermal degradation. With the S-PVC samples, however, we found a weak relation between thermal instability and the content of $(Cl_L)_{phenol}$ (Fig. 2), and consequently also a weak relation to Structure I. There is obviously also a weak relation between instability and Structure II. Other labile structures must be more important for the thermal stability. Neither phenolysis nor bromination is therefore an adequate method for the determination of the relevant thermolabile structures.

The conclusion that Structure I has no major influence on the thermal stability is strengthened by the investigation of the U-PVC samples. For these samples, there is a strong relation between thermal instability and $(Cl_L)_{phenol}$ (Fig. 2). Compared to the S-PVC fractions, the U-PVC samples show not only inferior thermal stability but also much lower content of Structure I. This is revealed by the much lower intensity of the doublet at 4.05 ppm in Fig. 12. The difference in unsaturation is also obvious in the area 5.0-6.0 ppm where U-PVC shows a broader and less distinct spectrum of the olefinic protons. It is also evident that the concentration of Structure II is similar in both U-PVC and S-PVC. In U-PVC, the peak at 3.75 ppm is considerably larger. This peak is assigned to chloromethyl groups

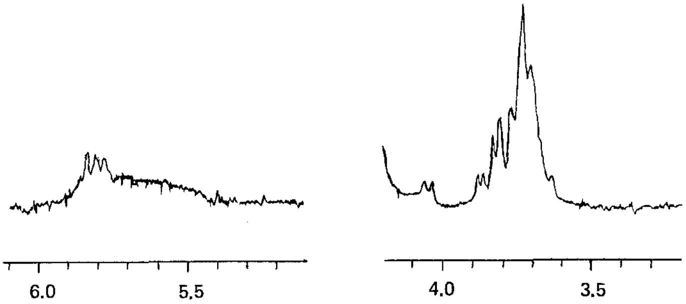


FIG. 12. Parts of ^{1}H-NMR spectrum (200 MHz) of a low molecular weight U-PVC fraction (from Sample A2) with about the same molecular weight as the S-PVC Sample C1.

and $\sim\!\sim CH_2-CH_2Cl$ ends. The NMR measurements on U-PVC also indicate that the above-mentioned structure differences increase with decreasing monomer pressure.

It is not likely that the differences in end structure are the reason for the inferior thermal stability of U-PVC. Further work is therefore in progress to reveal which labile structures are formed due to changes in the reaction pattern at monomer starvation. We will soon report on studies of anomalous structures along the chains, such as internal double bonds and branch points.

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