

Formation of anomalous structures in PVC and their influence on the thermal stability:

2. Branch structures and tertiary chlorine*

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Branch structures were determined in fractions of a commercial suspension of PVC (S-PVC) and experimental PVC samples obtained at subsaturation conditions (U-PVC). The analyses were performed with ^{13}C n.m.r. spectroscopy at 50.31 MHz after reductive dehalogenation with tributyltinhydride. With increasing monomer starvation U-PVC was found to have an increasing amount of butyl and long chain branches (LCB). A polymer prepared at 55°C and 59% of the saturation pressure of vinylchloride had 3.4 butyl branches and 2.0 LCB per 1000 monomer units. In the S-PVC series the total content of these two structures varied between 0.5 and 1.0 per 1000 monomer units. By using tributyltindeuteride as reducing agent the structure of the butyl branches could be determined as $\sim\text{CHCl}-\text{CH}_2-\text{CCl}(\text{CH}_2-\text{CHCl}-\text{CH}_2-\text{CH}_2\text{Cl})-\text{CH}_2-\text{CHCl}\sim$. A major part of the LCB points also contained tertiary chlorine. The formation of LCB is suggested as occurring after abstraction of hydrogen from the polymer chain by macroradicals and chlorine atoms. The latter will lead to LCB points with tertiary hydrogen and internal double bonds. The rate of dehydrochlorination at 190°C in nitrogen could be related to the amount of tertiary chlorine (correction coefficient=0.97). It was assumed that tertiary chlorine is the most important labile structure in PVC.

Keywords Poly(vinyl chloride); thermal stability; branch structure; tertiary chlorine; carbon 13 nuclear magnetic resonance; reductive dehalogenation

INTRODUCTION

In a series of investigations we have determined different irregular structures in PVC and evaluated their effect on its thermal stability. We have compared fractions of a commercial suspension PVC (S-PVC) with PVC polymerized at reduced monomer pressure (U-PVC). As previously reported, we have used subsaturation polymerization as a model for the polymerization conditions after the pressure drop in a conventional polymerization²⁻⁴, assuming that polymers with reduced stabilities are formed during these stages.

With decreasing monomer pressure the U-PVC showed decreased thermal stability and molecular weight. In the S-PVC series there was only a weak relation between molecular weight and the rate of dehydrochlorination (deHCl).

The first paper⁵ in this series was concerned with the determination of labile chlorine by phenolysis, double bonds by bromination and end group structures by n.m.r. spectroscopy. Although the U-PVC and S-PVC series showed large differences in thermal stability they could not be distinguished from each other by the chemical methods used. The n.m.r. measurements showed that the most frequent unsaturated end group in the S-PVC samples 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). Phenolysis and bromination give a measure of the 1-chloro-2-alkene end groups. Neither this group nor the saturated 1,2-dichloro-alkane end group influence the thermal stability to any appreciable extent.

Also we could not detect any labile structures in the U-PVC samples. The content of unsaturated end groups does not change but the proportion of 1-chloro-2-alkene end groups decreases with decreasing monomer pressure while the concentration of 1,2-dichloro-alkane end groups seems to be the same as for S-PVC. We also found $\sim\text{CH}_2-\text{CHCl}$ end groups, increasing with the monomer starvation at polymerization.

As a consequence of these measurements we believe that the heat sensitive structures are internal allylic or tertiary chlorine. In this paper we present the result of our studies of the branch structures in the S-PVC and U-PVC samples. The analysis was made using ^{13}C n.m.r. after reductive dehalogenation by tributyltinhydride (Bu_3SnH). To reveal the position of chlorine in the original PVC, reductions were also performed with tributyltindeuteride (Bu_3SnD).

EXPERIMENTAL

Materials

The same polymer samples were used here as in the previous investigation⁵. The U-PVC samples were polymerized at 55°C and at monomer pressures between

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

Table 1 Series A, U-PVC^a

Sample No.	P/P_0	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	$\frac{LCB}{1000VC}$	$\frac{deHCl}{dt} \times 10^2$ (%/min)
A 1	0.59	13.7	50	2.8	5.47
A 2	0.59	17.3	72	3.1	4.42
A 3	0.67	17.6	62	2.7	5.05
A 4	0.67	20.0	75	1.7	3.85
A 5	0.67	20.7	70	2.0	3.95
A 6	0.75	21.5	98	3.2	3.80
A 7	0.75	23.4	95	2.1	3.25
A 8	0.85	25.8	89	3.4	3.03
A 9	0.85	35.9	113	0.9	1.70
A10	0.92	40.7	137	1.1	2.00

^a Same sample designation as in ref. 2Table 2 Series C, S-PVC^a

Sample No.	Extracted from	Extraction system	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	$\frac{LCB}{1000VC}$	$\frac{deHCl}{dt} \times 10^2$ ^b (%/min)
C-3	C-7	acetone	19.3	50	1.0	1.55
C-4	C-7	acetone/THF (95 : 5)	21.0	43.5	0.6	1.20
C-5	C-7	acetone/THF (90 : 10)	26.8	54	0.6	1.11
C-6	C-7	acetone/THF (83 : 17)	33.4	69	0.4	0.93
C-7	—	—	46.3	102	0.3	1.38
C-8	C-4 residue	complete dissolution	60.1	113	0.3	1.05

^a Same sample designations as in ref. 2^b Rate of dehydrochlorination at 190°C in nitrogen expressed in percent of original HCl evolved per minute

59–92% of the saturation pressure of vinyl chloride at 55°C (see Table 1). The fractions of S-PVC were obtained by extraction from a commercial S-PVC (Pevikon S687, KemaNord AB, Sweden) polymerized at 55°C (see Table 2).

Bu_3SnH was obtained by reacting polymethylhydrosiloxane with bis-tributyltin oxide⁶. The experimental details have been given previously⁷. Bu_3SnD was obtained from Aldrich and was used after distillation (about 86°C at 2 mm Hg).

To check the ¹³C chemical shifts of the carbons associated with saturated chain ends, $n-C_{44}H_{90}$ (Fluka AG) was used. Commercial copolymers of ethylene and 1-butene, 1-hexene (Unifos AB, Sweden) or 1-octene (Dow Chemicals, USA) were used as references for the ethyl, butyl and hexyl branches, respectively.

Reductions

The reductive dechlorination was performed with Bu_3SnH as the reducing agent. We have modified the original two step method given by Starnes *et al.*⁸ to a one step method. By this procedure a chlorine content less than 0.1% is obtained in 6 h. The experimental details are as previously given⁷. The reductions with Bu_3SnD were performed in a similar way.

N.m.r. measurements

Proton decoupled ¹³C n.m.r. spectra were obtained with a Varian XL-200 spectrometer. Free induction decays with spectra windows of 8000 Hz were stored in 16 K computer locations with 32 bits wordlength. The tip angle was 65° and the pulse interval 10 s. Samples reduced with Bu_3SnH were observed at 120°C as 10–20% (w/v)

solutions in 1,2,4-trichlorobenzene with 25% benzene- d_6 to provide the deuterium lock. The number of scans accumulated was 8–10 000. The solution conditions for the samples reduced with Bu_3SnD were the same but the pulse interval was 3 s and the number of scans was around 80 000. The Fourier transformations were performed with floating point arithmetic. As reference the main methylene peak was used; 30.0 ppm *versus* TMS for hydride reduced samples and 29.85 ppm for deuteride reduced samples.

D.s.c. measurements

The melting behaviour of the reduced samples were studied with a Perkin-Elmer DSC-2 differential scanning calorimeter. The heating rate was 10 K min⁻¹ and the sample size 5 mg. All runs were performed in a nitrogen atmosphere. Before analysis all samples were given the same thermal treatment by heating to 150°C and cooling down to 0°C in a controlled manner.

RESULTS AND DISCUSSION

The presence of chlorine obscures the n.m.r. spectra of PVC to such an extent that the branching structure cannot be revealed. A reduction to the corresponding hydrocarbon is therefore usually performed. Earlier, $LiAlH_4$ was used as the reducing agent despite several drawbacks including side reactions. Reduction with Bu_3SnH does not give the latter complication and is much faster and more convenient. We have used a modification⁷ of the method introduced by Starnes *et al.*⁸

For the interpretation of the ¹³C n.m.r. spectra of the reduced PVC samples, the assignments given by Randall⁹ for polyolefins were used. To complement these

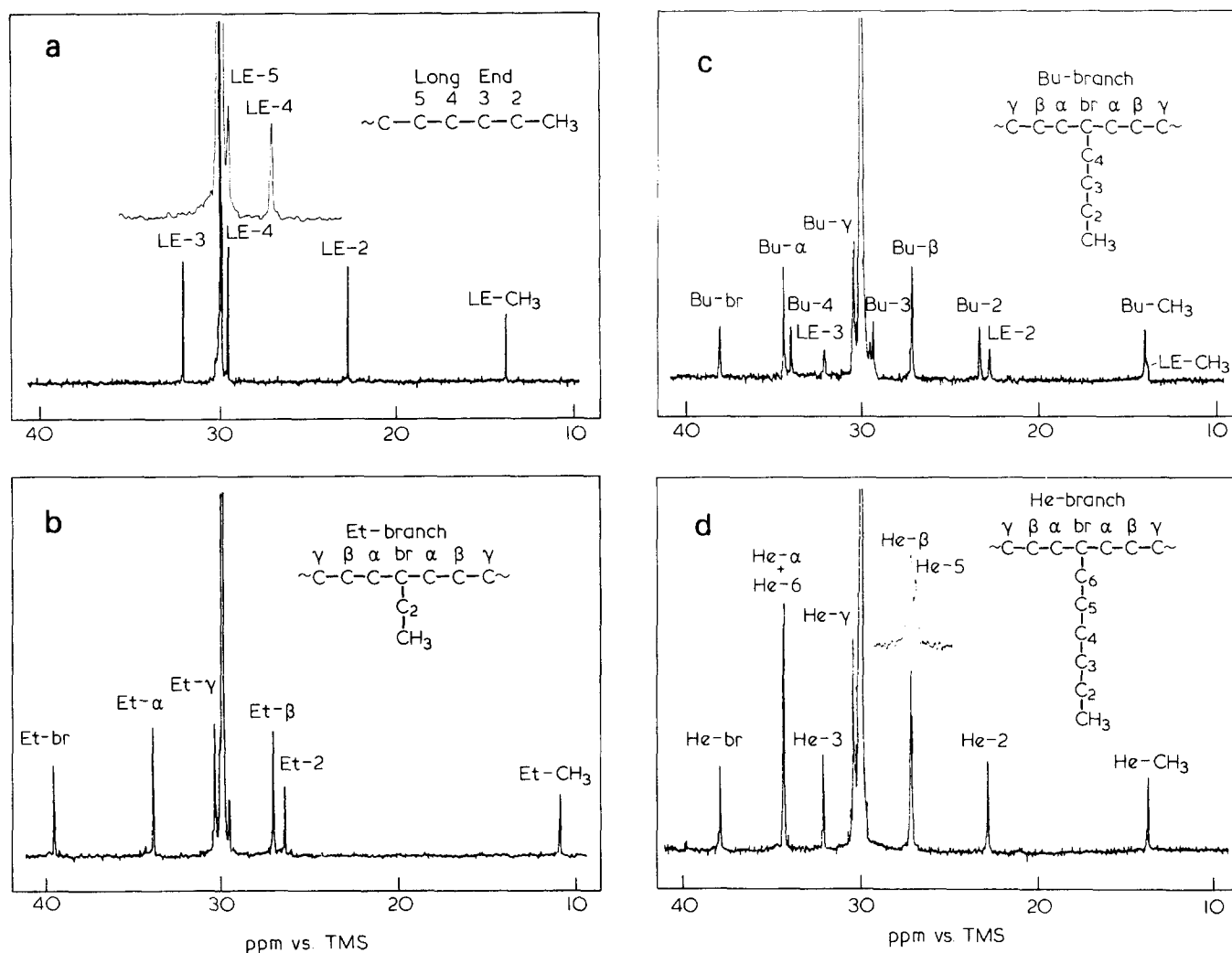


Figure 1 Proton decoupled ^{13}C n.m.r. spectra (50.31 MHz) of model compounds for long chain ends and branch structures. (a) $\text{N-C}_{44}\text{H}_{90}$, number of scans 100; (b) poly(ethylene-co-1-butene), ~ 18 ethyl/1000 C, 5000 scans; (c) poly(ethylene-co-1-hexene), ~ 5 butyl/1000 C, 11000 scans; (d) poly(ethylene-co-1-octene), ~ 10 hexyl/1000 C, 6000 scans

investigations, we investigated a straight chain hydrocarbon ($\text{n-C}_{44}\text{H}_{90}$) and ethylene-butene, ethylene-hexene and ethylene-octene copolymers. The spectra are shown in Figure 1. As shown in Table 3 there is a good agreement between our results and those reported by Randall.

Table 3 ^{13}C shifts for long chain ends and short chain branches expressed in ppm versus TMS

A Long chain ends ($\text{n-C}_{44}\text{H}_{90}$)										
	CH_3	2	3	4	5					
This work	14.06	22.88	32.17	29.60	29.95					
B Ethyl branches (poly(ethylene-co-1-butene))										
	CH_3	2	br	α	β	γ				
Randall ^a	11.19	26.79	39.68	34.09	27.30	30.40				
This work	11.15	26.64	39.59	33.97	27.27	30.48				
C Butyl branches (poly(ethylene-co-1-hexane))										
	CH_3	2	3	4	br	α	β	γ		
Randall ^a	14.13	23.37	29.76	34.09	38.10	34.48	27.26	30.44		
This work	14.12	23.38	29.47	34.05	38.08	34.45	27.25	30.49		
D Hexyl branches (poly(ethylene-co-1-octene))										
	CH_3	2	3	4	5	6	br	α	β	γ
Randall ^b	14.19	22.98	32.26	30.08	27.32	34.52	38.17	34.52	27.32	—
This work	14.09	22.91	32.20		27.18	34.45	38.12	34.45	27.23	30.48

^a Ref. 9

^b Ref. 11

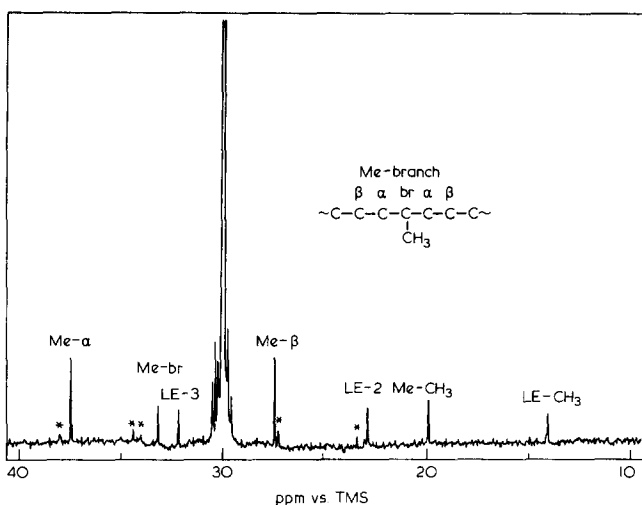
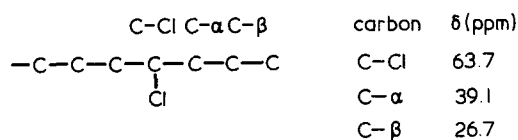


Figure 2 Proton decoupled ^{13}C n.m.r. spectrum of S-PVC (sample C-5) reduced with Bu_3SnH

For the straight chain alkane LE- CH_3 to LE-5 can be observed. The difference in chemical shift between the main peak and that of LE-5 is only 0.05 ppm. A similar situation is obtained for He-5 which is shifted 0.05 ppm upfield compared with He- β . This separation has been observed earlier¹⁰. In the same way carbon number 5 in a heptyl branch should be shifted 0.05 ppm upfield compared with the heptyl γ carbons in the main chain. This should in principle allow a distinction of branches up to 7 carbons compared with the accepted length of 5 carbons¹¹. However, we feel that this small shift difference can only be used for the identification of ethylene-1-olefin copolymers. As branches longer than 2 carbons have almost identical chemical shifts for the β and γ carbons respectively, it is doubtful if this separation is possible in a polymer with several types of branching, i.e. a conventional high pressure low density polyethylene.

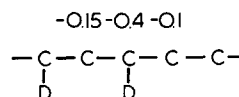
In Figure 2 a typical spectrum of reduced S-PVC is given. This spectrum is very similar to those published earlier^{8,12-14}. Besides the main peak some small peaks related to end structures and branches are seen. A complete reduction is verified by the absence of peaks at 62.7 (not shown), 39.1 and 26.7 ppm due to isolated chlorinated structures¹⁴:



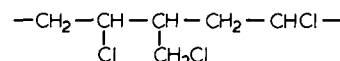
In accordance with earlier workers it was found that the methyl branches are the only branch structure that can be observed to any appreciable extent. The content is about 4 per 1000 monomer units (1000 VC), independent of the molecular weight (see Table 4). However, a closer inspection also reveals some minor peaks, marked by stars, hardly distinguishable from the noise. These peaks will be discussed in further detail below.

To establish the position of chlorine in the original polymer, reductions were carried out with Bu_3SnD . As the spin quantum number of deuterium is 1, a carbon

labelled with a deuterium will appear as a triplet. Further information about the deuterated structure can be obtained from the isotope shift¹⁵. The following approximate upfield shifts (ppm) are expected:



A typical spectrum of a S-PVC reduced with Bu_3SnD is shown in Figure 3. The presence of CH_2Cl branches in the original PVC is revealed by the triplet around 19.6 ppm. The complete microstructure round the chloromethyl group is:



This is confirmed by the unsplit peak of the branch carbon and by the partial splitting of the peaks associated with the α and β carbons. Further confirmation is obtained from the isotope shifts (see Table 5). These results are in accordance with those obtained by Bovey and coworkers^{13,16}.

Table 4 Content of methyl branches in hydride reduced S-PVC samples

Sample No.	$M_n \cdot 10^{-3}$	$\frac{-\text{CH}_3}{1000 \text{ VC}}^a$
C-3	19.3	4.2
C-4	21.0	4.4
C-5	26.8	4.1
C-6	33.4	3.8
C-7	46.3	4.0
C-8	60.1	4.0

^a Determined from Me- α , Me- β and Me-br

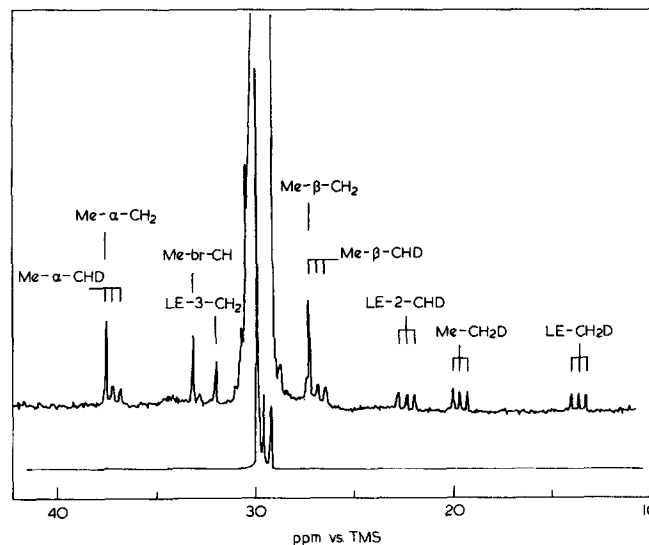
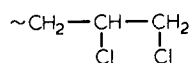


Figure 3 Proton decoupled ^{13}C n.m.r. spectrum of S-PVC (sample C-5) reduced with Bu_3SnD

Table 5 ^{13}C shifts in ppm versus TMS in S-PVC reduced with Bu_3SnH and Bu_3SnD

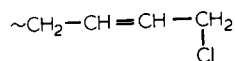
Carbon	Chemical shift		Isotope shift (ppm)	Substitution pattern
	Bu_3SnH -reduced	Bu_3SnD -reduced		
Me- CH_3	19.94	CH_2D 19.66	-0.28	1 attached
Me-br	33.21	CH 33.11	-0.10	1 neighbour
Me- α	37.51	CH_2 37.42	-0.08	1 neighbour
		CHD 37.10	-0.41	1 attached
Me- β	27.44	CH_2 27.31	-0.13	1 neighbour
		CHD 27.10	-0.34	1 attached
LE- CH_3	14.08	CH_2D 13.66	-0.42	1 attached, 1 neighbour
LE-2	22.88	CHD 22.43	-0.45	1 attached, 1 neighbour
LE-3	32.17	CH_2 32.02	-0.15	2 neighbours

In agreement with their result our measurements also show that the most frequent saturated end group is:



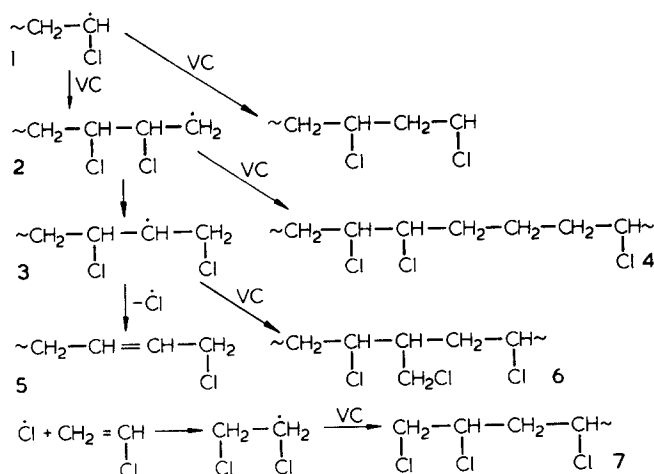
This structure has also been demonstrated to be the most frequent by ^1H n.m.r. on unreduced PVC^{1,5,17,18}. According to our measurements the content of such groups is 0.8–0.9 per molecule.

By ^1H n.m.r. it has been shown that the most frequent unsaturated end group is^{1,5,17}:



We found about 0.7 such groups per molecule.

The classical view of vinyl chloride polymerization and especially the chain transfer to monomer by a direct reaction between monomer and a macroradical, cannot account for these end groups. To explain the formation of both the end groups and the chloromethyl branches the following scheme has been proposed^{1,5,15,19}:



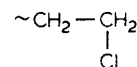
The head-to-head addition (1 to 2) followed by 1,2-Cl migration (2 to 3) was originally proposed by Rigo *et al.*²⁰ for the formation of short branches in PVC. Recently, this path in the reaction mechanism was confirmed by Starnes *et al.*¹⁵ favouring the alternative route *via* 1,2-H migration from an ordinary macroradical^{17,21}.

As the relation between deHCl rate and number average molecular weight is weak for the S-PVC samples (see Table 2), the two end groups obviously have little deleterious effect on the thermal stability⁵. The chloromethyl group does not contribute to the instability either, according to Park *et al.*²² On the contrary, they report a stabilizing effect of these groups. Therefore, the reactions given above do not seem to give any explanation for the formation of labile structures in conventional PVC.

As structure 4 is not believed to be formed¹⁵ the only expected change in this reaction scheme at subsaturation polymerizations should be due to the balance between the two possible reactions from 3. With decreasing monomer concentration a decreasing content of the chloromethyl branches as well as a decreasing molecular weight would result. In contrast, a direct radical transfer to monomer from a macroradical would show little influence of the monomer concentration on the molecular weight in the same as what is observed for the influence of the initiator concentration. The observed decrease in molecular weight of PVC with decreasing monomer pressure is thus in accordance with the new reaction mechanism²³.

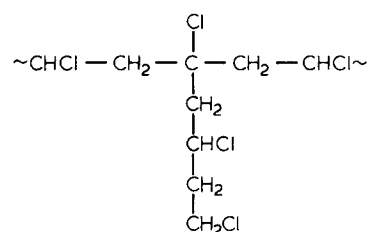
However, a decrease in monomer concentration will also result in other changes in the polymerization reactions^{1,5}. It is e.g. demonstrated by a decreasing relative amount of 1-chloro-2-alkene end groups at reduced pressures. At the same time the content of 1,2-dichloro-alkane end groups is unchanged indicating that the chlorine atom is the chain transfer agent also at subsaturation conditions.

The ^1H n.m.r. measurements of U-PVC showed an increasing amount of the following saturated chain end structure:



In this way the total amount of saturated chain ends becomes higher than 1 per molecule, already at a fairly low degree of starvation. At the same time the number of unsaturated chain ends is close to 1 per molecule. The increased amount of long chain branching²⁻⁴ cannot fully account for the increased content of end groups. An increase of the content of short chain branches would, however, be a reasonable explanation.

At the PVC symposium in Cleveland¹ we stated that the increased amount of end groups in the U-PVC samples were due to butyl groups. Their complete microstructure was also given:



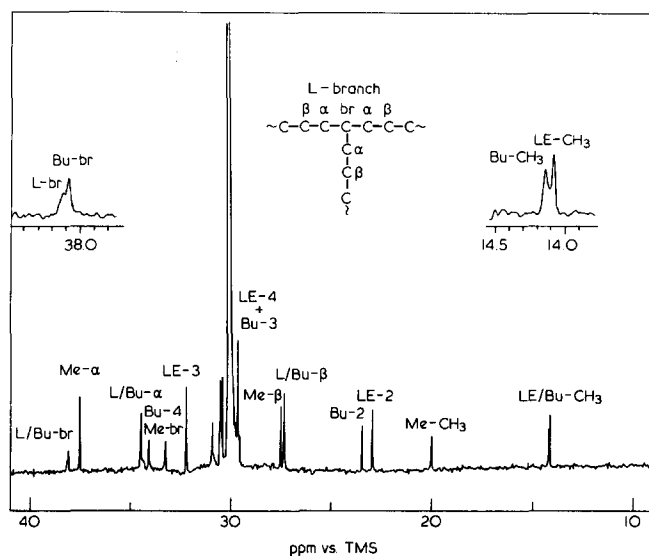


Figure 4 Proton decoupled ^{13}C n.m.r. spectrum of U-PVC (sample A1) reduced with Bu_3SnH

This branch structure was revealed by the ^{13}C spectra of U-PVC reduced with Bu_3SnH and Bu_3SnD , respectively. A typical spectrum of a hydride reduced U-PVC is shown in Figure 4.

Compared with the S-PVC spectra, e.g. Figure 2, the U-PVC spectra are more complex. Apart from the peaks originating from reduced chloromethyl branches there are also peaks associated with butyl groups. The most obvious ones are the Bu-2 and Bu-4 carbons at 23.39 and 34.13 ppm, respectively. Bu- CH_3 is also clearly seen as separated from LE- CH_3 , (compare with models in Table 3). Bu-3, however, is not separated from LE-4. The content of butyl branches can be determined by the content of Bu-2 or Bu-4 carbons. It is also possible to use the content of Bu/LE- CH_3 after subtraction of the content of long chain ends obtained from LE-2 or LE-3, but this value will be somewhat inaccurate due to longer relaxation times²⁴.

The peaks originating from the branch, α and β carbons in the main chain have more or less the same shift for butyl and longer branches. Pentyl groups are not present as no peak from Pe-3 is found at 32.75 ppm¹¹. However, g.p.c. and viscometry measurements have shown that long chain branches (> 50 carbons) are present in U-PVC²⁻⁴. Our ^{13}C n.m.r. measurements confirm this. There is an excess of L/Bu- α and L/Bu- β compared with the number of butyl groups. In most cases, the content of long chain branches, i.e. 6 carbons or longer, was found to be lower than that of butyl groups. The peak at 38.09 ppm was therefore assigned to Bu-br and the shoulder on the downfield side to L-br²⁵. This is in accordance with the shift difference of 0.05 ppm for He-5 and He- β respectively LE-5 and $-(\text{CH}_2)_n-$.

The spectra shown in Figures 2 and 4 were obtained by data treatment optimal for high resolution and they were not used in the quantitative evaluation. In that case a peak broadening weighting function was applied before the Fourier transformation in order to obtain an optimal signal-to-noise ratio. In these spectra peak heights for carbons in the same structure are very similar in contrast to what is occasionally found in the 'high resolution' spectra, e.g. Bu-2 and Bu-4 in Figure 4.

The results for the quantitative determinations are given in Table 6. As shown the content of butyl and long chain branches increase with decreasing monomer pressure. The content of chloromethyl groups, however, is slightly lower in U-PVC than in S-PVC. The latter is in accordance with the expected influence of subsaturation conditions in the newly suggested reaction scheme for chain transfer to monomer (see above).

As mentioned earlier, the spectra of the S-PVC samples contain some minor peaks. A comparison with a spectrum of U-PVC shows that these peaks are associated with butyl and/or long chain branches. The low content of these structures in the S-PVC samples does not allow an accurate quantitative determination of the two separate structures. Therefore, based on the α and β carbons, an estimation of the sum of the two branches is given in Table 6 for the S-PVC samples.

In a previous paper⁷ we used the melting point of the reduced samples as a measure of the chlorine content. This implies that the content of branches is constant. In the present material this assumption is not valid. As the content of chlorine is low, <0.1%, the melting point will instead give a measure of the content of butyl and long chain branches (see Figure 5).

The values of long chain branches obtained by ^{13}C n.m.r. spectroscopy of reduced U-PVC are clearly lower than the values obtained by g.p.c.-viscometry (see Figure 6). The implication of this result on the calculation of long chain branches from g.p.c. and viscosity measurements will be discussed in a separate paper.

The position of chlorine in the original U-PVC was established by ^{13}C n.m.r. of deuteride reduced samples. A typical spectrum is given in Figure 7. The lower trace shows the principal $-\text{CH}_2-$ and $-\text{CHD}-$ resonances. The latter is split into a triplet centred at 29.57 ppm with a one bond scalar coupling of 19 Hz. The chemical shift due to one attached deuterium is -0.43 ppm. The methylene carbons are shifted -0.15 ppm due to the two neighbouring deuterium atoms¹⁵.

The upper trace is the same spectrum plotted at a higher magnification. As expected the reduced chloromethyl

Table 6 Content of branches in the U-PVC and S-PVC series determined by ^{13}C n.m.r.

Sample No.	Chloromethyl	Branches			
		1000 VC	1,2-dichlorobutyl	LCB	
U-PVC	A 1	3.4	3.4	—	2.0
	A 2	3.5	4.0	—	0.8
	A 3	3.8	2.8	—	2.0
	A 4	3.6	2.2	—	1.0
	A 5	3.6	2.9	—	1.1
	A 6	3.6	3.0	—	0.7
	A 7	3.8	2.8	—	1.4
	A 8	3.7	2.0	—	1.2
	A 9	3.8	0.7	—	1.2
	A10	4.0	1.6	—	0.5
S-PVC ^a	C-3	4.2	—	1.0	—
	C-4	4.4	—	0.8	—
	C-5	4.1	—	0.7	—
	C-6	3.8	—	0.7	—
	C-7	4.0	—	0.9	—
	C-8	4.0	—	0.5	—

^a In the S-PVC series, it was not possible to obtain an accurate separation between butyl branches and LCB (see text)

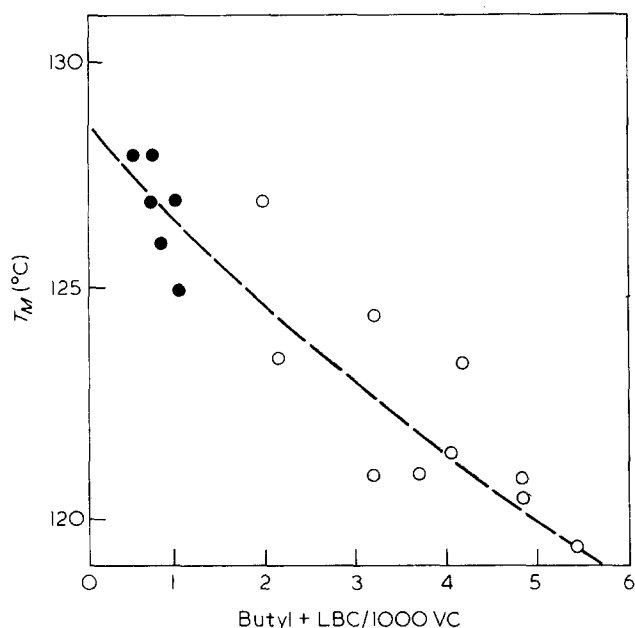
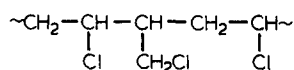
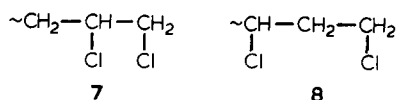


Figure 5 Melting point, T_M , of the reduced polymers as a function of the total content of butyl and long chain branches

branches give a completely split signal from the methyl carbons. The other carbons associated with the chloromethyl branch structures show a similar behaviour as in S-PVC. Evidently, the chloromethyl branches in U-PVC are identical with those in ordinary PVC:



The LE and Bu methyl carbons also show split signals, which is evidence for chloromethyl structures in the original PVC. In contrast to S-PVC, U-PVC shows an almost unsplit LE-2 resonance. The shift is -0.17 ppm indicating two neighbouring deuterium atoms. In addition, compared with the spectrum of the hydride reduced sample, the relative intensity is considerably lower. This points to the existence of a certain fraction of $-\text{CHD}-$ at the LE-2 position. The content of original $-\text{CHCl}-$ is too low to be clearly seen after deuterium labelling although some minor peaks indicate a triplet. The situation at the LE-3 resonance is similar. A singlet with reduced intensity is seen at 32.02 ppm, i.e. with a shift of -0.15 ppm indicating two neighbouring deuterium atoms. The triplet from LE-3-CHD can not be seen. These facts indicate that two saturated long chain ends are present in the unreduced U-PVC:



The short pulse interval used for the deuteride reduced samples does not allow an exact calculation of the content of these structures. A semiquantitative evaluation shows that the relative content of structure **8** increases with decreasing pressure. In a sample polymerized at 75% of the saturation pressure, the concentrations of the two

structures are about the same. At 59% saturation pressure about 60% of the saturated chain ends have 1,3-dichloroalkane structure (**8**) and 40% 1,2-dichloroalkane structure (**7**). Starnes *et al.*²⁶ have reported that in a sample obtained by batch polymerization at 100°C the relative concentrations were 25% for **8** and 75% for **7**. Both the ^{13}C measurements on deuteride reduced polymers and the ^1H n.m.r. investigations of the original PVC⁵ show that structure **7** is the major saturated chain end structure in ordinary PVC obtained at normal temperatures.

As mentioned above Bu- CH_3 is split into a triplet. The behaviour of Bu-3 cannot be observed as this signal is included in the peaks of the principal carbons. However,

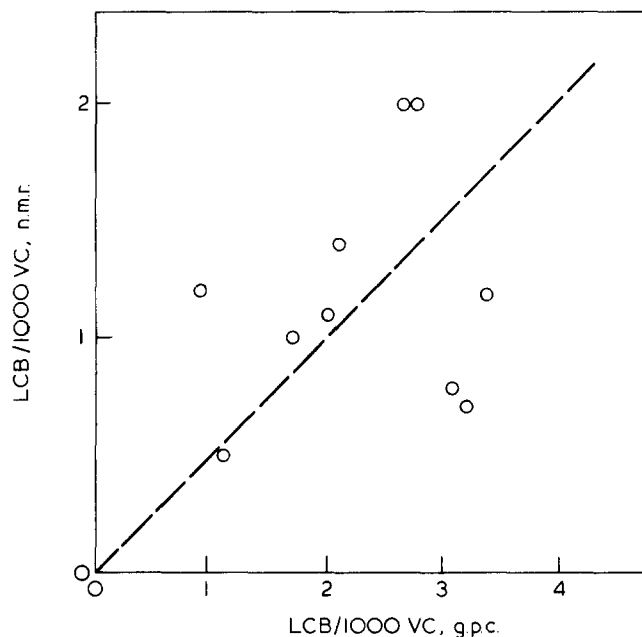


Figure 6 Relation between the content of LCB determined by ^{13}C n.m.r. of reduced polymer and LCB determined by g.p.c. viscometry of the original PVCs

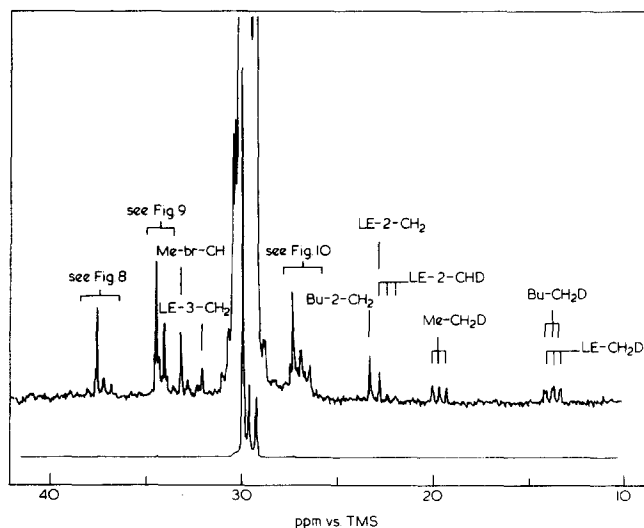
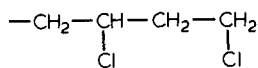
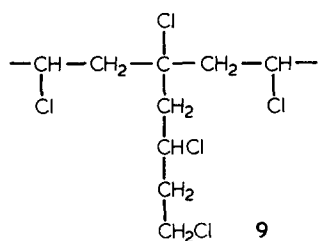


Figure 7 Proton decoupled ^{13}C n.m.r. spectrum of U-PVC (sample A1) reduced with Bu_3SnD

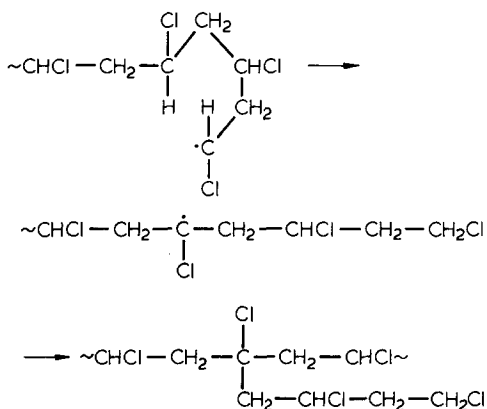
as neither Bu-2 nor Bu-4 are split and as they are shifted -0.14 ppm compared with the hydride reduced sample, the following structure of the butyl group can be assigned:



The signal for Bu/L- α is for the major part unsplit with a isotope shift of -0.14 ppm. As there are about twice as many butyl branches as long chain branches, the Bu- α carbons should be $\text{---CH}_2\text{---}$ with two neighbouring chlorine atoms. The changes for the two peaks of the β carbons point to a mixture of $\text{---CH}_2\text{---}$ and ---CHD--- with a rather high content of the latter. The α and β carbons will be discussed in more detail below. The branch carbons in the butyl and long chain branches do not give any clear signal. The most reasonable explanation is that chlorine is attached to these carbons in the original sample. The resulting triplet for the deuteride reduced sample is shifted towards the Me- α signal and will therefore be difficult to observe. In Figure 8 this part of the spectrum is shown with a larger magnification. Some weak signals are in fact found at the expected positions of a deuterium labelled branch carbon in butyl branches. Altogether these observations conclusively show that the complete microstructure of the butyl group is:



This structure is what could be expected from a back-biting mechanism as suggested by Bobey and Tiers²⁷:



This reaction competes with the propagation and should increase in frequency at reduced monomer concentration. As mentioned above this is in accordance with our observations (see Table 6).

Accordingly, using U-PVC and commercial S-PVC we were able to prove the existence of butyl groups and to establish their microstructure^{1,2,5}. Butyl branches have also been observed in U-PVC prepared at atmospheric

pressure²⁸. In earlier papers Starnes and coworkers did not find any evidence of butyl groups in ordinary PVC^{8,12,14}. To increase the probability of branch formation they prepared PVC at 100°C . This polymer was reported to contain 2,4 LCB/1000 VC and an equal amount of ethyl branches¹⁶. At the Cleveland meeting the LCB points (2.0/1000 VC) were reported to contain tertiary chlorine²⁶. It was also suggested that the polymer might contain butyl branches. Recently, a content of 0.6 LCB/1000 VC and 1.8 butyl branches per 1000 VC was given for the same polymer²⁹. The structure of the butyl branches given above was confirmed.

Starnes *et al.*²⁶ have stated that ethyl branches are formed, not only at elevated, but also at normal polymerization temperatures, being 1.6/1000 VC at 100°C and 0.4/1000 VC at 43°C . Ethyl branches might be formed by simple back-biting or by a more complex mechanism as suggested by Willbourn³⁰ for polyethylene. Reasonably, the concentration of ethyl branches should increase with decreasing monomer concentration in the same way as the concentration of butyl branches. However, we cannot find any evidence of ethyl branches in our U-PVC samples which were obtained at 55°C and 59–92% saturation pressure. In no case are there peaks at the expected frequencies for Et- CH_3 (11.2 ppm) or Et-br (39.6 ppm) as demonstrated in Figure 4. A polymer prepared at 80°C and 60% of the saturation pressure did not show any evidence of such branches either³¹. It is therefore unlikely that ethyl branches are formed in PVC at conditions normal to commercial polymerization, i.e. in the temperature range $40^\circ\text{--}70^\circ\text{C}$.

As mentioned above, Starnes *et al.*²⁶ suggested that LCB points contain tertiary chlorine:

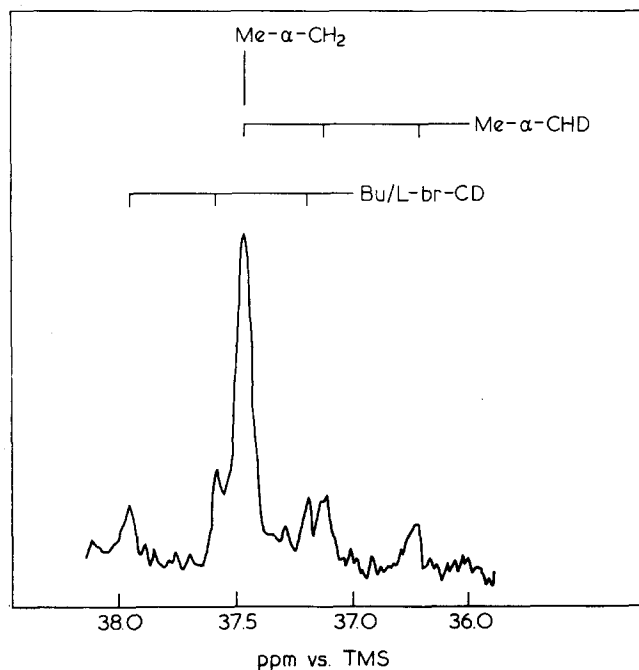
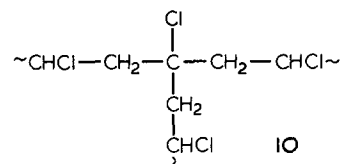


Figure 8 Part of the spectrum in Figure 7 showing L/Bu-br and Me- α carbons

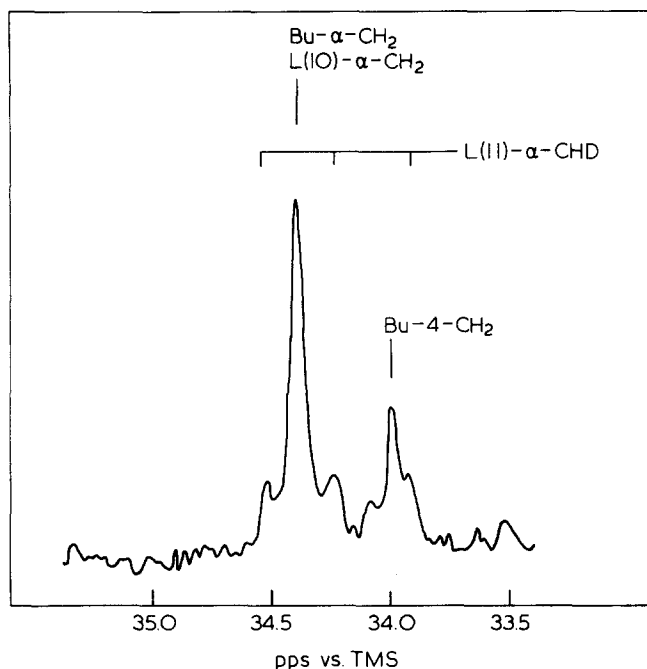
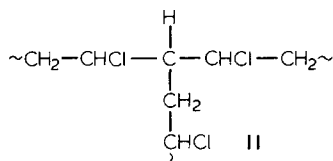


Figure 9 Part of the spectrum in Figure 7 showing L/Bu- α and Bu-4 carbons. For designation of LCB structure see text

The assignment was based on the investigation of the 100°C polymer containing 2 LCB/1000 VC. In a more recent paper²⁹ only 0.6 LCB together with 1.8 butyl branches per 1000 VC were reported. In this case the signals associated with the long branches will be difficult to observe in the spectrum of the deuteride reduced sample.

In U-PVC obtained at low pressure the situation for the determination of this structure is more favourable (see Table 6). The presence of a very weak signal at 37.95 ppm (Figure 8) shows that the long chain carbon branches contain considerable chlorine, i.e. according to structure 10. The α -carbons of this structure should give a singlet at 34.35 ppm (common to Bu- α). The majority of the L/Bu- α carbons can also be found in one peak at 34.37 ppm (see Figure 9). There are, however, also some minor peaks. Their positions are in reasonable agreement with those expected for α -carbons originating from a long chain branch point with tertiary hydrogen:



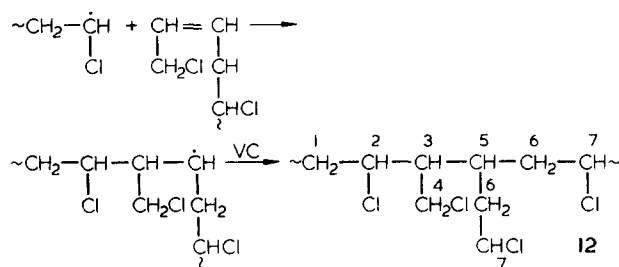
After deuteride reduction L- α -CHD should give a triplet shifted -0.3 ppm and with a spacing of 19 Hz while L- α -CH₂ should be shifted about -0.07 ppm. In Figure 9 a triplet can be seen at about the expected position. If this assignment is correct the peak heights would indicate that about 1/3 of the long chain branch points carry tertiary hydrogen.

The signals related to the β -carbons in the deuteride reduced sample do not give any clear evidence for the structure of the long chain branch points. A major reason for this is that the Bu- β resonance is a triplet (see Figure

10). The shoulder at 27.12 ppm is *per se* in accordance with L- β -CH₂ in structure 11.

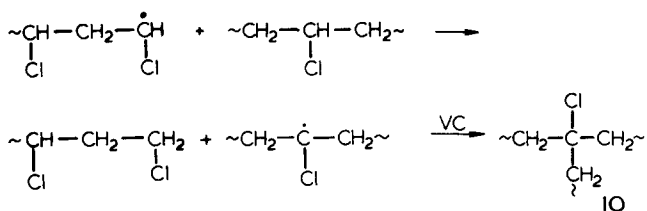
Two main alternatives are usually given in explaining the formation of long chain branches in PVC; copolymerization between vinylchloride and unsaturated chain ends and propagation from a macroradical obtained by proton abstraction from a polymer chain.

Berens³² suggested copolymerization with vinyl end groups, at that time assumed to be the main unsaturated chain end. As discussed above, the main unsaturated chain end is the 1-chloro-2-alkene structure. Therefore, copolymerization would be an unlikely route to long chain branches. If, however, this reaction did occur the following structure would be formed:



After reduction resonances according to Table 7 would be found in the ¹³C spectrum. We did not find any indications of this structure in our U-PVC samples, see e.g. Figure 4. Copolymerization between vinyl chloride and 1-chloro-2-alkene chain ends can thus be ruled out as the mechanism for the formation of long chain branches in PVC.

Abstraction of a proton from the polymer is usually ascribed to chain transfer to a polymer from a macroradical. For PVC such a transfer would be selective³³ and lead to LCB points with tertiary chlorine:



A mechanism involving hydrogen abstraction by macroradicals is supported by the fact that we find an increasing amount of 1,3-dichloroalkane long chain ends in U-PVC together with an increasing amount of LCB. Based on similar results obtained with a 100°C polymer, Starnes *et al.*²⁶ suggested this mechanism to be the main route to LCB in PVC. Attack by e.g. initiator radicals would also give LCB points with tertiary chlorine. This reaction is, however, not likely with water soluble initiators.

The new scheme for chain transfer to monomer implies chlorine atoms as the chain transfer agent. This very active species must also be considered for chain transfer to polymer, especially at monomer starved conditions. Due to its high reactivity the attack by a chlorine atom would be rather unselective. Chlorination experiments indicate, however, that the methylene groups are preferably

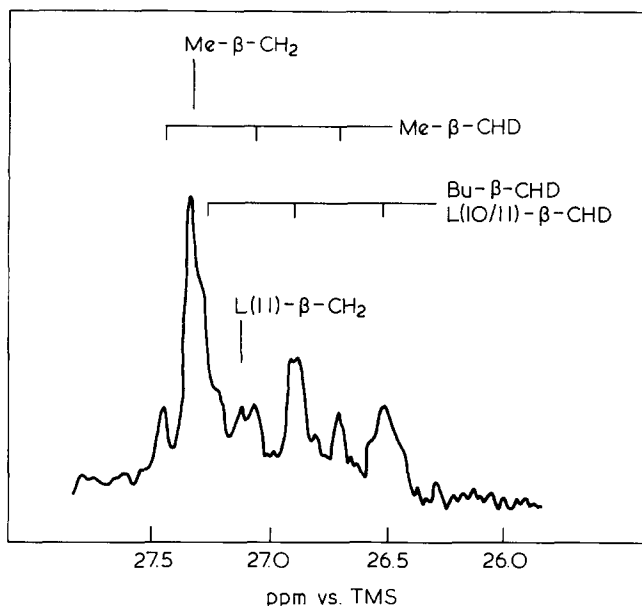


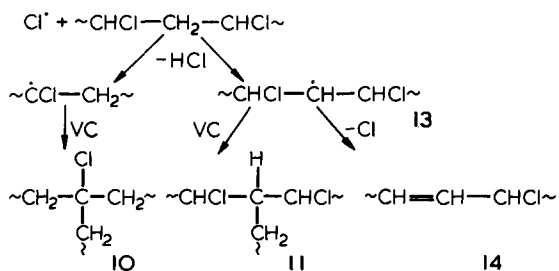
Figure 10 Part of the spectrum in Figure 7 showing L/Bu-β and Me-β carbons. For designation of LCB structure see text

Table 7 Expected chemical shifts of a structure involving a methyl branch adjacent to a long chain branch point. The carbon designations are given in the text

Carbon No.	Expected shift ^a (ppm)	Carbon No.	Expected shift (ppm)
1	27.5	5	40.6
2	34.5	6	31.8
3	35.0	7	27.8
4	26.1	—	—

^a According to Lindeman and Adams parameters

attacked³⁴. Besides the formation of LCB we also suggest that this transfer to the polymer is responsible for the increased formation of internal double bonds at subsaturation conditions^{1,35}:



The two possible reactions for radical 13 are very similar to the reactions for radical 3 in the reaction mechanism for chain transfer to monomer. Radical 13 can propagate and long chain branches are formed (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). For radical 3, the relation between propagation and chlorine repulsion is about 5:1 at saturated conditions and 55°C. Consequently, if transfer to polymer by chlorine is

responsible for the formation of internal double bonds it is most likely that LCB including tertiary hydrogen are formed.

This mechanism is supported by our observations of the structure of the LCB points. Braun and Sonderhof³⁶ reported that hydrogen chloride is formed in polymerizations of vinyl chloride after the pressure drop. A further indirect support is the relation, $\bar{M}_n \propto [M]^{0.6}$, reported earlier²⁶. The new scheme for chain transfer to monomer implies a linear decrease of the molecular weight with decreasing monomer concentration. When LCB are formed after attack by chlorine atoms the decrease in \bar{M}_n is counteracted by the reduction in the number of polymer molecules formed.

Thermal stability

If the thermal stability of PVC polymerized at subsaturation conditions is compared with the molecular weight, one might draw the conclusion that the end groups of U-PVC have a very deleterious effect. This is illustrated in Figure 11 where the rate of dehydrochlorination (deHCl) is plotted versus the inverse of \bar{M}_n , i.e. the concentration of end groups. In the U-PVC series the thermal stability seems to strongly depend on the number of end groups. For the S-PVC series on the other hand, this relation is weak. The same picture is obtained if the rate of deHCl is plotted versus the number of labile chlorine as determined by phenol substitution^{1,5}.

However, in the first paper in this series⁵ we showed that both S-PVC and U-PVC gave the same relation between the number of labile chlorine atoms and the inverse of \bar{M}_n . The phenolysis can thus not be taken as a measure of the tendency to deHCl. At least in the S-PVC series the phenolysis mainly determines the 1-chloro-2-alkene end groups which obviously do not influence the thermal stability to any appreciable extent.

The difference between S-PVC and U-PVC, as demonstrated in Figure 11, can instead be explained by tertiary and internal allylic chlorine atoms. When the

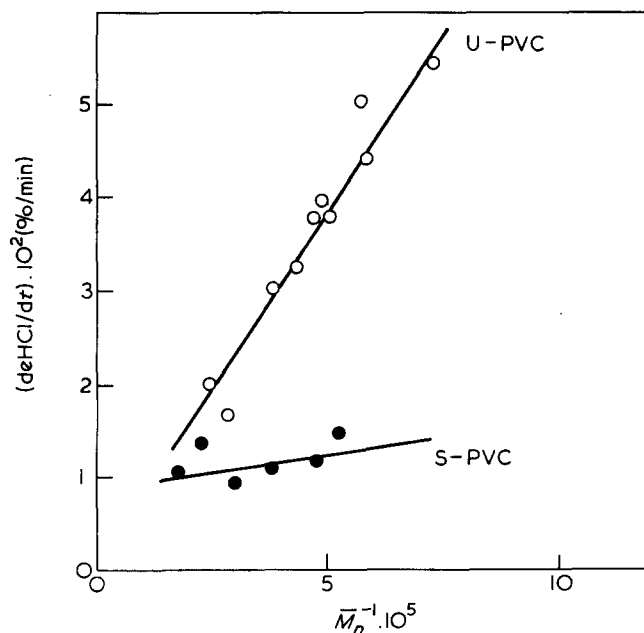


Figure 11 Relation between rate of dehydrochlorination at 190° in nitrogen the reverse of \bar{M}_n ; ○, U-PVC; ●, S-PVC

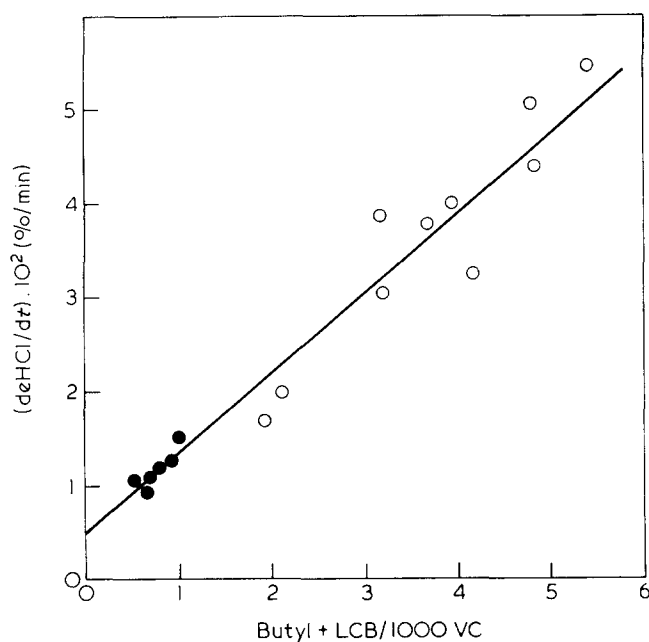


Figure 12 Relation between rate of dehydrochlorination and the amount of tertiary chlorine given as the total content of butyl and long chain branches (see text)

monomer pressure decreases the molecular weight decreases as well as the thermal stability (see Table 1). However, at the same time the number of tertiary chlorines (Table 4) and internal allylic chlorines^{1,35} increase. The adverse effects of such structures have been demonstrated by both low³⁷ and high molecular weight models^{32,38,39}. From experiments with copolymer of vinyl chloride and 2-chloro-propene, Berens³² stated that the presence of 1 tertiary chlorine per 1000 monomer units could *per se* explain the instability of PVC.

The present material allows a direct comparison between thermal stability and content of tertiary chlorine in PVC. For the U-PVC series it has been shown that tertiary chlorines are primarily associated with butyl groups and that long chain branch points mainly contain tertiary chlorines. It is reasonable to believe that the S-PVC series show the same behaviour but the low concentration does not even allow a separation between butyl and long chain branches in this series. The combined concentrations of these two branches are therefore taken as a measure of the content of tertiary chlorine. As shown in Figure 12 the relation between the rate of dehydrochlorination and the content of tertiary chlorine is clear. Contrary to what was obtained in the comparison between the rate of dehydrochlorination and the content of labile chlorine determined by phenolysis all samples coincide along the same line (correlation coefficient = 0.97).

As is reported separately^{1,35} the amount of internal double bonds also increases with decreasing monomer pressure. Naturally, the increasing amount of internal allylic chlorine will contribute to the decreasing thermal stability of U-PVC. However, the amount of tertiary chlorine is about five-times higher than the amount of allylic chlorine. In our opinion tertiary chlorine is thus the most important labile structure. The concentration of such groups in ordinary PVC is about 0.5–1 per 1000 monomer units. Even such a low amount has a very serious effect on the thermal stability (see Figure 12).

CONCLUSIONS

In the polymerization of vinyl chloride, long chain branches are formed after abstraction of hydrogen from the polymer chain. Abstraction by a macroradical is assumed to lead to LCB points with tertiary chlorine. Attack of chlorine atoms on the methylene group is suggested to result in the formation of LCB points with tertiary hydrogen and internal double bonds with allylic chlorine. A major part of the LCB points contain tertiary chlorine. Back-biting leads to the formation of butyl branches with tertiary chlorine. In the investigated fractions of ordinary PVC the content of tertiary chlorine is about 0.5–1 per 1000 VC. With increasing monomer starvation the frequencies of the side reactions increase. In a polymer prepared at 59% of the saturation pressure, the content of tertiary chlorine has increased to about 5 per 1000 VC. The tendency to dehydrochlorination is strongly related to the amount of tertiary chlorine. It is assumed that tertiary chlorine is the most important labile structure in PVC.

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