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Degradation of Poly(vinyl chloride) with Increased Thermal Stability

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ABSTRACT: Poly(vinyl chloride) (PVC) was treated with ethanol, trimethylaluminum, and dibutyltin maleate in order to substitute labile chlorine. The degradation behavior of the modified samples was compared with that of an ordinary suspension PVC and a PVC obtained by anionic polymerization. All modified samples and the anionic PVC showed the same behavior when degraded in pure nitrogen. Besides a decreased rate of dehydrochlorination, the polyenes became shorter. Degradation in atmosphere containing HCl resulted in a higher dehydrochlorination rate and longer polyenes for all samples with improved heat stability, except for the sample treated with trimethylaluminum which exhibited excellent thermal stability. The results showed that the polyene sequence distribution depends on the presence of HCl in the sample during degradation. The content of incorporated methyl groups in the alkylated sample was determined to about 1 per 1000 monomer units. Furthermore, the content of tertiary chlorine was reduced to less than 10% of that of unreacted PVC. It is concluded that the enhanced thermal stability is caused by removal of labile chlorine.

Introduction

The thermal stability of poly(vinyl chloride) (PVC) is substantially lower than what could be expected from the nominal structure, and the reason for the low stability has been the subject of many investigations; see, e.g., refs 1–3. In our previous work we were able to correlate the amount of labile chlorine, tertiary and internal allylic chlorine, to the dehydrochlorination rate.[4-6] One of the key factors was that we studied PVC samples with increased contents of labile chlorine, which were obtained by polymerization at reduced monomer concentration. According to our results tertiary chlorine is the most important defect in PVC. In agreement with other reports,[1,7,8] the results also indicated that secondary chlorine is unstable at the temperatures in question; i.e. random initiation will occur. Although the importance of labile chlorine is supported by other groups, several publications have dealt with other labile sites, e.g. the ketoallylic group[9] and certain labile conformation (GTTG$^-$) of isotactic triads.[10-12]

Many attempts have been made to improve the thermal stability of PVC by decreasing the amount of labile structures. Kolinsky et al.[13-15] have studied polymerization of vinyl chloride initiated by butyllithium. This is supposed to be an anionic polymerization in which chain transfer to polymer, intra- and intermolecular, is unlikely. This would give a lower content of labile chlorine, and the dehydrochlorination rate of such polymers is indeed substantially lower than that of ordinary PVC.[16] Elimination of labile structures formed during polymerization is another way to improve the stability. This can be achieved by substitution of thermally labile chlorine by more strongly bonded groups, e.g. mercaptide,[17,18] alkyl,[19,22] and carboxylate[23] groups. Besides a decreased rate of dehydrochlorination, modification of PVC results in an extra bonus: the discoloration at a given level of dehydrochlorination becomes less.[16,21,22,24-26]

Another point which has been discussed is the influence of HCl during degradation. Nowadays, there is overhelming experimental evidence that HCl catalyzes the thermal degradation (see, e.g., ref 3). In previous papers[16,25] we have discussed the degradation of PVC with improved thermal stability in pure nitrogen and in atmosphere containing HCl. In the presence of HCl both the rate of dehydrochlorination and the polyene sequence length increased and became almost the same as that observed for normal PVC. We did also suggest a mechanism for HCl catalysis of the propagation step in the degradation of PVC.

In this paper we present the results of our continued investigation of PVC with increased heat stability, obtained both by modification and anionic polymerization. Several different reagents were used to substitute labile chlorine. PVC treated with trimethylaluminum showed excellent stability, and this sample was therefore investigated in more detail. The main aspects are the influence of HCl and the content of tertiary and allylic chlorine.

Experimental Section

PVC Samples. Five types of PVC samples have been used in this investigation; see Table I. Samples A and D were obtained by suspension polymerization at 56 °C in a 5-L stainless steel reactor. Poly(vinyl alcohol) was used as a suspending agent and dicetyl peroxydicarbonate as initiator. Vinyl chloride was kindly supplied by Norsk Hydro Plast AB, Sweden. After water had been added, air was removed by five cycles of evacuation and purging with extra pure nitrogen (<2 ppm O_2). All additions were made under a nitrogen blanket. The polymerization was stopped shortly after the pressure drop. In the polymerization of sample D a small amount (0.1%) of dibutyltin bis(isobutyl maleate) was added to the vinyl chloride before the polymerization, according to refs 27 and 28.

Sample B was obtained by treating sample A with ethanol/water (1:1) for 2 h at 150 °C in an autoclave.

Sample C was obtained by reacting sample A with Me_3Al (20% in hexane solution, Alfa Products) in benzene slurry according to Mitani et al.[22] To a stirred suspension of 5 g of PVC (sample A) in 35 mL of benzene was added 2.5 mmol of Me_3Al. The reaction was carried out at 80 °C for 1 h. The resultant mixture was cooled to 0 °C, poured into 0.8 L of acidified methanol, filtered, and dried.

Sample E, generously supplied by AKZO, Holland, was polymerized with butyllithium as initiator ($M_n = 9.3 \times 10^3$, $M_w = 163 \times 10^3$), essentially according to Kolinsky et al.[13-15]

Thermal Degradation. Thermal degradation experiments were performed with two different types of apparatus. A Perkin-Elmer TGS-2 was used to measure the weight loss of the PVC samples during degradation in HCl/nitrogen (15% HCl). The heating rate was 320 °C/min up to 190 °C where the temperature was held constant. The sample weight was about 10 mg. Degradations were also performed in a specially designed apparatus described earlier.[29] Due to minor changes in the equipment the obtained dehydrochlorination rate was about 25%

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Table I
Investigated Samples

sample	reagent	
A		
B	C_2H_5OH	after polymerization
C	$(CH_3)_3Al$	after polymerization
D	$(C_4H_9)_2Sn(OCOR)_2$	during polymerization
E		anionic polymerization

lower than in refs 6 and 29. Bulk samples (150 mg) were heated at 190 °C in either nitrogen (<5 ppm O_2) or HCl/nitrogen (15% HCl) atmospheres. The dehydrochlorination was followed conductometrically when nitrogen atmosphere was used. In the case of an atmosphere containing HCl the degradation time to a certain degree of dehydrochlorination was calculated from the degradation rate obtained in the TGS experiments. The rates of dehydrochlorination are expressed as evolved HCl, as a percentage of the theoretical amount, per minute. For both techniques the deviation for repeated measurements was ±5%.

Polyene Sequence Distribution. The polyene sequence distributions in the degraded samples were determined qualitatively by UV-visible spectroscopy. The absorbance spectra were obtained from tetrahydrofuran solutions with a Perkin-Elmer 554 spectrophotometer. The solutions (4 g/L) were carefully prepared under nitrogen using peroxide-free THF.[30]

Determination of Internal Double Bonds. The number of internal double bonds (or polyene sequences) in the samples was determined by following the changes in M_n caused by the ozone oxidative cleavage of all double bonds. The ozonolysis was performed principally according to Michel et al.[31] PVC (500 mg) was dissolved in cyclohexanone (100 mL), and a small amount of methanol was added to facilitate the cleavage of the ozonide formed. The ozonolysis was performed at −20 °C for 2 h, and the polymer was recovered by precipitation in methanol and dried in vacuum for 24 h. The number of internal cleavages per 1000 monomer units ($(C{=}C)_n/1000$ VC) was calculated from the number-average molecular weight before ($M_{n,0}$) and after (M_n) the oxidative treatment:

$$(C{=}C)_n/1000\ \mathrm{VC} = 62500(1/M_n - 1/M_{n,0})$$

Determination of Branches. The number of branches was determined by ^{13}C NMR after reduction. The reductive dechlorinations were performed in a mixture of tetrahydrofuran and xylene with Bu_3SnH as the reducing agent. The experimental details have been given earlier.[32] Proton-decoupled ^{13}C NMR spectra were obtained with a Varian VXR-300 spectrometer. The reduced samples were observed at 110–120 °C as 10–15% (w/v) solutions in 1,2,4-trichlorobenzene with 20% benzene-d_6 to provide the deuterium lock. The acquisition time was 2 s, the tip angle 60°, and the pulse interval 8 s. The number of scans accumulated was 8000–9000.

^1H NMR Measurements. Spectra were obtained with a Varian VXR-300 spectrometer. The samples were observed at room temperature as 5% (w/v) solutions in acetone-d_6/CS_2 (1:1). About 1000 scans were accumulated.

Determination of Tacticity. The tacticity was measured from ^{13}C NMR spectra recorded on a Varian XL-300 spectrometer. The samples were run at 50 °C as 8–10% solutions in mixtures of tetrahydrofuran/benzene-d_6 (volume ratio 4:1). The acquisition time was 5 s, the tip angle 50°, and the pulse interval 1 s. The number of scans accumulated was 10 000.

Results and Discussion

By polymerization of vinyl chloride at reduced monomer pressure we have earlier investigated the relations between polymerization conditions and formation of defect structures with low stability.[4-6] We found that decreased monomer concentration favors formation of tertiary chlorine associated with ethyl, butyl, and long-chain branches as well as internal double bonds with allylic chlorine. The amount of tertiary chlorine does also increase with the temperature while the number of internal double bonds shows a weak tendency to decrease.

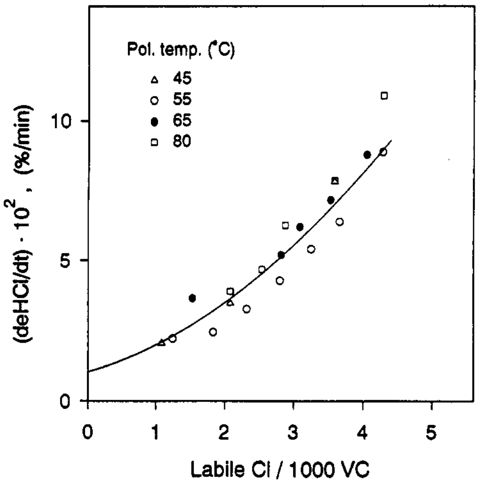


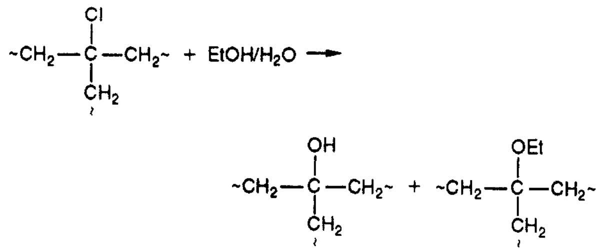
Figure 1. Relation between rate of dehydrochlorination and the content of labile chlorine for PVC obtained at subsaturation conditions (after ref 6).

It was further possible to correlate the rate of dehydrochlorination with the content of tertiary and internal allylic chlorine; see Figure 1. It should be noted that all samples follow the same relation independently of the polymerization temperature (45–80 °C). This indicates that tacticity should be of less importance. Another conclusion is that the nominal structure of PVC should not be stable at the applied conditions (190 °C, N_2), as indicated by the extrapolation to zero content of defects.

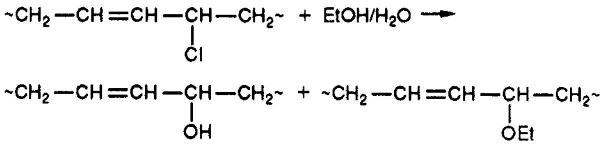
An important assumption for the extrapolation in Figure 1 is that each initiation point would give the same number of HCl losses at all dehydrochlorination rates; i.e. the polyene sequence distribution should be independent of the stability of the sample. In another work we have, however, shown that the polyenes become shorter in samples with increased stability compared to ordinary PVC.[16,25] This would imply that the rate of dehydrochlorination for a sample with zero content of labile chlorine would be still lower than that indicated by the extrapolation in Figure 1.

To obtain a PVC with decreased content of defects, and thus increased stability, there are in principle two possible routes, both discussed in the literature. Ideally, one should choose a polymerization mechanism that gives less defects than the ordinary radical polymerization of vinyl chloride. The other possibility is to accept the polymer obtained by radical polymerization and afterward substitute the labile chlorine to obtain another, more stable, group. Most of the work discussed in refs 16 and 25 was done on a sample that was reacted with a tin carboxylate; i.e. the latter strategy had been chosen to increase the stability. No direct proof for the substitution was given and the general applicability of the results can of course be discussed. We have now applied a number of different techniques to obtain PVC with improved heat stability in order to study if the effects mentioned above are generally valid. In some cases it has also been possible to analyze the structure of the used samples in more detail.

An obvious way to substitute labile chlorine is to use a postpolymerization process. We have tried two different techniques reported earlier, reaction with ethanol/water (sample B) and with alkylaluminum (sample C). Treatment with ethanol/water at about 150 °C has been discussed by Suzuki.[33] He considers that tertiary and internal allylic chlorine are substituted:

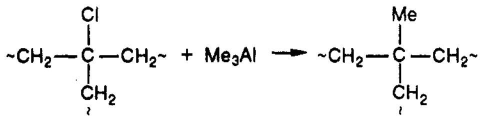


$$\sim CH_2-\underset{\underset{\wr}{CH_2}}{\overset{Cl}{C}}-CH_2\sim + EtOH/H_2O \longrightarrow \sim CH_2-\underset{\underset{\wr}{CH_2}}{\overset{OH}{C}}-CH_2\sim + \sim CH_2-\underset{\underset{\wr}{CH_2}}{\overset{OEt}{C}}-CH_2\sim \quad (1)$$

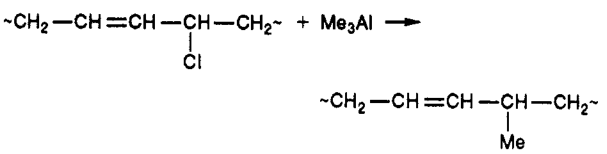


$$\sim CH_2-CH=CH-\underset{Cl}{CH}-CH_2\sim + EtOH/H_2O \longrightarrow \sim CH_2-CH=CH-\underset{OH}{CH}-CH_2\sim + \sim CH_2-CH=CH-\underset{OEt}{CH}-CH_2\sim \quad (2)$$

Reaction with alkylaluminums has been studied by several groups.[19-22] It is expected that a labile carbon–chlorine bond is replaced by a carbon–carbon bond, which should be the most favorable one from a stability point of view:



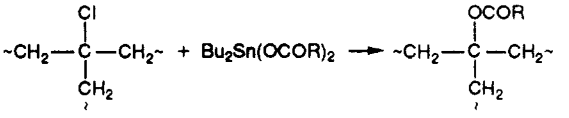
$$\sim CH_2-\underset{\underset{\wr}{CH_2}}{\overset{Cl}{C}}-CH_2\sim + Me_3Al \longrightarrow \sim CH_2-\underset{\underset{\wr}{CH_2}}{\overset{Me}{C}}-CH_2\sim \quad (3)$$



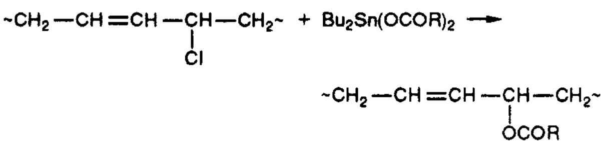
$$\sim CH_2-CH=CH-\underset{Cl}{CH}-CH_2\sim + Me_3Al \longrightarrow \sim CH_2-CH=CH-\underset{Me}{CH}-CH_2\sim \quad (4)$$

Another possibility would be to use the chemistry that is working for stabilizers added in processing of PVC. According to the Frye–Horst theory[23] the most important function of a metal carboxylate would be to substitute the labile chlorine with the carboxylate group. Starnes and co-workers[17,18,34-36] have reacted PVC with alkyltin mercaptide and/or thiols in solution at elevated temperatures and obtained PVC which shows a much lower degradation rate than that of the original polymer. Similar to the reactions discussed above, the reaction conditions that have to be applied to achieve the improvement would probably be too costly for commercial application.

We have therefore looked at a possibility to perform the substitution reaction during polymerization. In the patent literature there are several suggestions that heat-stable PVC could be obtained by adding a typical stabilizer in the reactor.[27,28] In most cases, however, rather large amounts of reactant are used (about 1%), and it can therefore be regarded as a way to effectively disperse the stabilizer. In the case of the PVC sample with improved stability used in our earlier investigation[16,25] quite small amounts (0.1%) of a tin carboxylate were used. Using dibutyltin maleate, this technique has been applied in this work as well (sample D). The following reactions are expected to occur:



$$\sim CH_2-\underset{\underset{\wr}{CH_2}}{\overset{Cl}{C}}-CH_2\sim + Bu_2Sn(OCOR)_2 \longrightarrow \sim CH_2-\underset{\underset{\wr}{CH_2}}{\overset{OCOR}{C}}-CH_2\sim \quad (5)$$



$$\sim CH_2-CH=CH-\underset{Cl}{CH}-CH_2\sim + Bu_2Sn(OCOR)_2 \longrightarrow \sim CH_2-CH=CH-\underset{OCOR}{CH}-CH_2\sim \quad (6)$$

The effect of these reactions was first tested by measuring dehydrochlorination at 190 °C in N_2. Besides the reference sample (A) and the substituted samples (B–D), a PVC obtained by polymerization with butyllithium as initiator (E) was included. All five samples exhibited the same general behavior; see Figure 2. After an apparent induction period, mainly caused by the time to reach thermal equilibrium and the dead volume in the system, linear plots were obtained and the slope can be taken as a measure of the stability; see Table II. All modified samples (B–D) and the anionic PVC (E) show increased thermal stability compared to the reference sample of ordinary PVC. It should be pointed out that blank experiments without active reactant only caused minor changes in the dehydrochlorination rate of the reference sample.

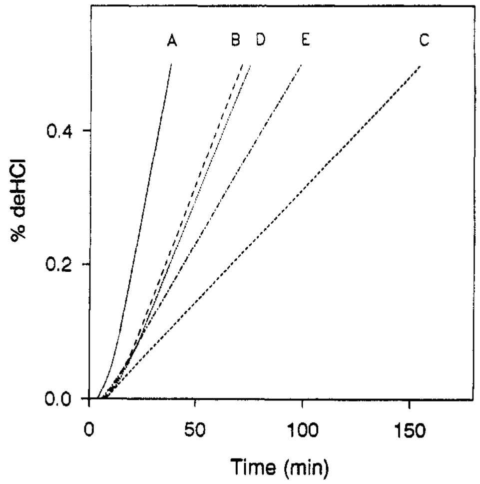


Figure 2. Degree of dehydrochlorination versus degradation time for samples A–E.

Table II
Dehydrochlorination Rate at 190 °C

	% deHCl/min × 10^3	
sample	nitrogen[a]	HCl[b]
A	17	18
B	8.4	
C	3.2	2.7
D	8.0	18
E	5.5	11

[a] Conductometric system. [b] Thermogravimetric system.

The improved stability indicates decreased content of labile chlorine. A comparison with Figure 1 would in principle allow an estimation of the expected amount of labile chlorine. Due to minor changes in the equipment we obtain about 25% lower values today. In the case of samples B, D, and E the dehydrochlorination rate is not as low as what could be expected for PVC without labile sites. Possible reasons might be reactivity of the introduced groups or eventual unreacted labile structures. For the sample obtained by heat treatment with EtOH (B) a slight discoloration even indicated that elimination reactions may be active during the substitution reaction. This sample was therefore excluded from the continued experiments.

It is generally supposed that if the polymerization of vinyl chloride can be made to take place via an anionic mechanism,[13-15,37] then it could be expected that the resulting structure would be perfect with few, if any, defects. The rate of dehydrochlorination of sample E is also low, although not exceptionally low. To obtain information about the most important defect, branches with tertiary chlorine, sample E was reduced, and the resulting hydrocarbon was analyzed with ^{13}C NMR; see Figure 3. Except for the main peak due to $-CH_2-$, some

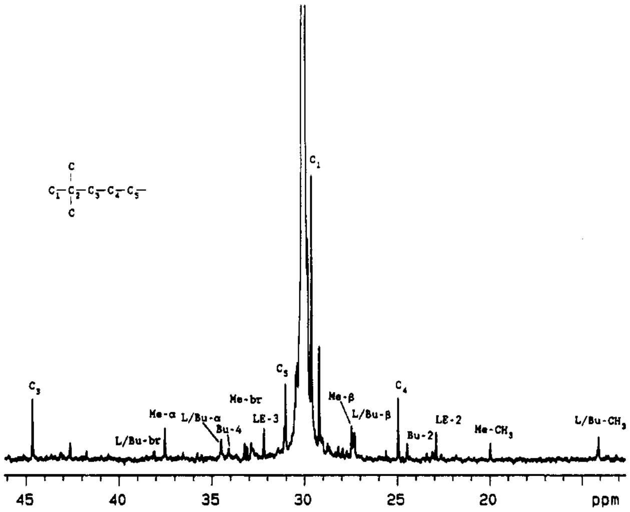
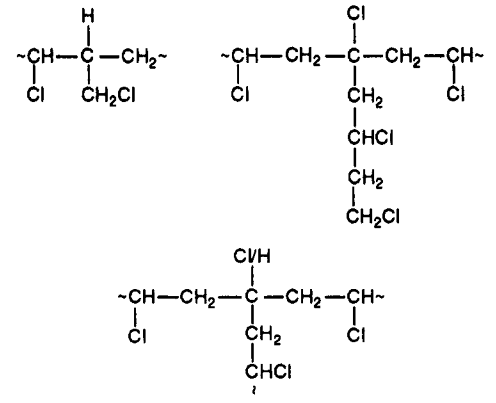


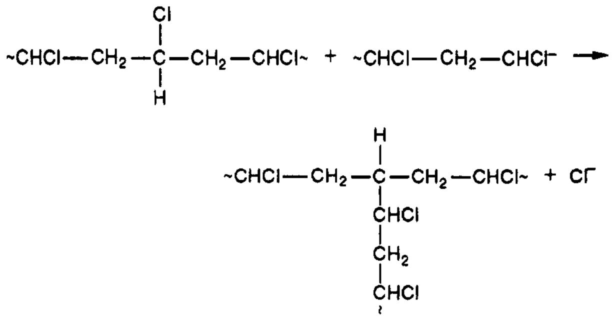
Figure 3. Proton decoupled ^{13}C NMR spectrum of anionic PVC (sample E) reduced with Bu_3SnH.

minor peaks can be seen; the most dominating at 25, 29, 31, and 45 ppm can be assigned to 2,2′-dimethyl-substituted alkyl chain ends.[38] Obviously, *tert*-butyllithium has been used as initiator. There are, however, other peaks which can be assigned to branch structures. One set corresponds to methyl groups (CH_3 at 20.0 ppm, CH_3-β at 27.4 ppm, CH_3-br at 33.2 ppm, and CH_3-α at 37.5 ppm), and the content is about 1.5/1000 VC. It is also possible to detect butyl and long-chain branches (L/Bu–CH_3 at 14.1 ppm, L/Bu-β at 27.2 ppm, Bu-4 at 34.1 ppm, L/Bu-α at 34.5 ppm, and L/Bu-br at 38.1 ppm). The contents of butyl and long-chain branches can be estimated to be about 0.4 and 0.9 per 1000 VC, respectively.

The presence of these branches is clear evidence that side reactions occur in polymerization of vinyl chloride initiated by butyllithium. The ^{13}C NMR spectrum obtained after reduction with Bu_3SnH does, however, only allow an evaluation of the carbon skeleton in the original PVC sample. To obtain the chlorine substitution pattern, the ^{13}C NMR spectrum must be recorded after reduction with Bu_3SnD[4,39] as well. In the case of radical polymerized PVC the methyl, butyl, and long branches have been found to have the following structures:



The chloromethyl branch is formed after head-to-head addition followed by 1,2-chlorine migration, and the butyl branch by back-biting, and the long branch by propagation after transfer to polymer by chlorine or a growing macroradical (see, e.g., ref 3). If the growing species is an anion instead, these reactions are, however, less likely. Considering that chloride ion is a good leaving group, we suggest that the long-chain branches are formed by a nucleophilic substitution reaction:



(7)

This reaction can be a reasonable explanation for the content of long-chain branches (0.9/1000 VC) compared to that in normal PVC (<0.5/1000 VC). It should further lead to tertiary hydrogen which is in agreement with the low dehydrochlorination rate.

For the two other branches it is much more difficult to put up a reasonable reaction mechanism without knowing the chlorine substitution pattern. It is per se likely that the methyl branches originate from $-CH_2Cl$ groups, in which case head-to-head addition could be a possibility also in anionic polymerization of PVC. Concerning the possible presence of tertiary chlorine it is, of course, tempting to compare the thermal stability of sample E with that of sample A. The rate of dehydrochlorination is about 30% of that of sample A, which contains 1.2 Cl_T/1000 VC. It is thus reasonable to assume that the butyl branches, 0.4/1000 VC, contain tertiary chlorine.

Besides the decreased rate of dehydrochlorination, the samples with improved thermal stability become less discolored when degraded in nitrogen. Similar results have been reported earlier by others.[21,22,24,26] This is demonstrated in Figure 4 by the UV spectra recorded after 0.4% dehydrochlorination. The samples with improved thermal stability (C–E) show much lower absorbance at longer wavelengths; i.e. the average sequence length of the polyenes is lower. In an earlier work[25] we have shown that the propagation of the polyenes is catalyzed by HCl; i.e. the polyenes become longer. The shorter polyenes observed in the PVC samples with improved stability can thus be related to a lower stationary concentration of HCl in the sample during degradation due to higher initial stability.

To investigate the influence of HCl on these samples we conducted degradation experiments in nitrogen with 15% HCl. For obvious reasons the rate of dehydrochlorination cannot be measured conductometrically when the carrier gas contains HCl. The degradation was instead followed by weight loss measurements using a thermogravimetric (TG) system. To obtain the same rate of dehydrochlorination for the reference PVC (A) in nitrogen in the TG as that measured in our ordinary apparatus at 190 °C, the temperature had to be set to 192 °C in the TG system. As shown in Table II the introduction of HCl did not influence the initial dehydrochlorination rate for the reference PVC sample to any noticeable extent. Neither was the distribution of the polyene sequences affected by adding HCl to the carrier gas; see Figure 5. For samples D and E, however, the rate of degradation was much higher in an atmosphere containing HCl compared to inert atmosphere. These samples also showed a marked increase in the absorbance at longer wavelengths; i.e. the polyenes became longer. This is illustrated in Figure 6 for sample D.

According to our earlier findings these results can be explained by HCl catalysis. The fact that the polyene distribution in the reference sample is not influenced by the presence of HCl in the carrier gas indicates, however, that there is a certain critical HCl concentration. In the

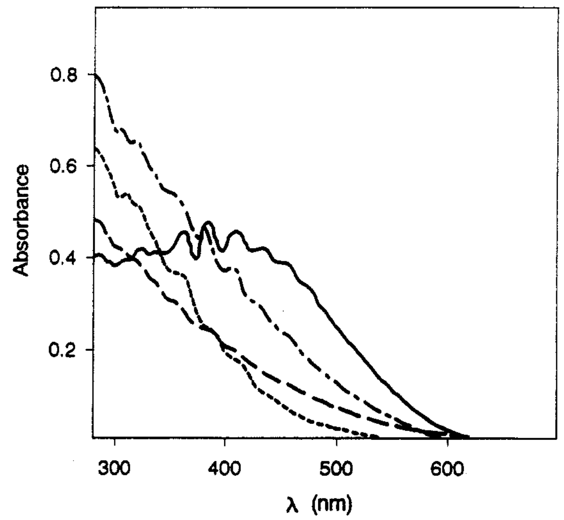


Figure 4. UV-visible spectra for samples degraded at 190 °C in nitrogen: sample A (—), C (- - -), D (– –), and E (— — —). All samples were degraded to 0.4% deHCl.

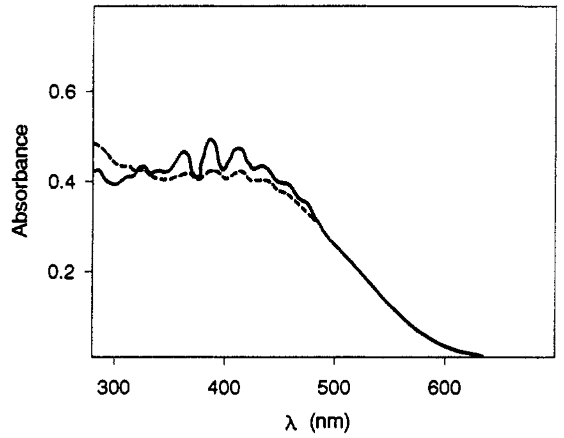


Figure 5. UV-visible spectra for sample A degraded at 190 °C in nitrogen (—) and in HCl (- - -). Both samples were degraded to 0.4% deHCl.

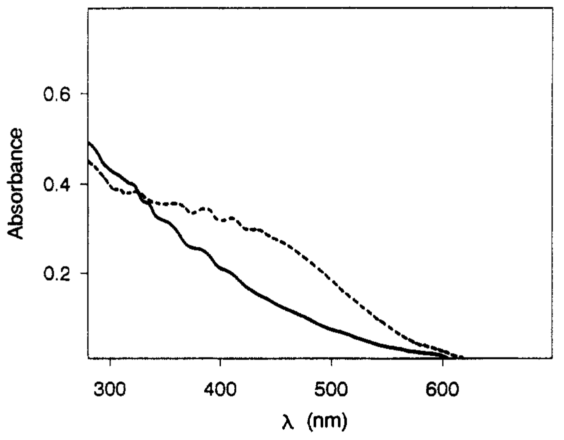


Figure 6. UV-visible spectra for sample D degraded at 190 °C in nitrogen (—) and in HCl (- - -). Both samples were degraded to 0.4% deHCl.

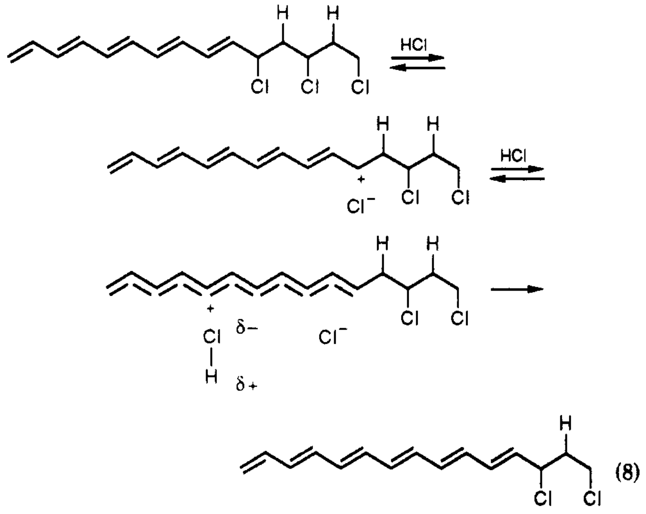
reference sample, the corresponding content of HCl in the polymer matrix would be reached already by the liberated HCl due to the higher dehydrochlorination rate. Addition of HCl to the carrier gas would then not affect the polyenes. For the improved samples, on the other hand, the lower dehydrochlorination rate in inert atmosphere implies a lower equilibrium concentration of HCl in the polymer. In this case increased HCl concentration in the atmosphere results in longer polyenes, except for sample C (reacted with Me_3Al) which will be discussed later.

Table III
Tacticity

sample	[rr][a]	[mr][b]	[mm][c]
A	0.33	0.49	0.18
E	0.33	0.48	0.19

[a] Fraction of syndiotactic triads. [b] Fraction of heterotactic triads. [c] Fraction of isotactic triads.

The increased length of the polyenes indicates that HCl catalyzes the propagation step. We have earlier suggested a mechanism for the HCl catalysis:[25]



(8)

At first the presence of HCl will increase the polarity and thus shift the first equilibrium to increased formation of ion pairs. HCl might also stabilize the polyenyl cation, which will tend to keep the chloride ion closer to the end of the sequence. Of course this would increase the possibility of abstracting a new proton. Both these effects will tend to increase the length of the polyene sequence.

An alternative explanation for the shorter polyene sequences in the improved samples is argued by Millan and his co-workers. In a series of papers they have stated that the instability of PVC to a large extent can be related to certain conformations, in particular GTTG⁻ in isotactic triads.[10-12,40-46,26] They have also worked with substitution reactions, e.g. with sodium benzenethiolate, and found changes in the UV spectra of degraded samples similar to those shown above. According to their opinion the shorter sequences are a result of replacement of the labile triads.[12,26,44]

As sample E was obtained by anionic polymerization, the UV spectrum obtained after degradation of this sample cannot be explained by removal of certain conformations. An NMR analysis further showed that the stereostructure of this sample was very similar to that of the reference sample (A); see Table III. The effect of HCl on the polyenes is also difficult to understand with this concept.

Another important issue is the amount of substitution needed to obtain the improved thermal stability. In a recent paper by Millan et al.[26] it is shown that the lowest dehydrochlorination rate (ca. 55% of the original) was obtained after 1% substitution for a certain sample. The results of the Me_3Al-treated PVC (sample C) are very interesting in this connection, and they will therefore be discussed in more detail. As mentioned above, the aim with alkylation is to substitute labile chlorine with methyl groups, i.e. replacement of labile carbon–chlorine bonds by thermally stable carbon–carbon bonds. The low rate of dehydrochlorination of sample C, ca. 20% that of the

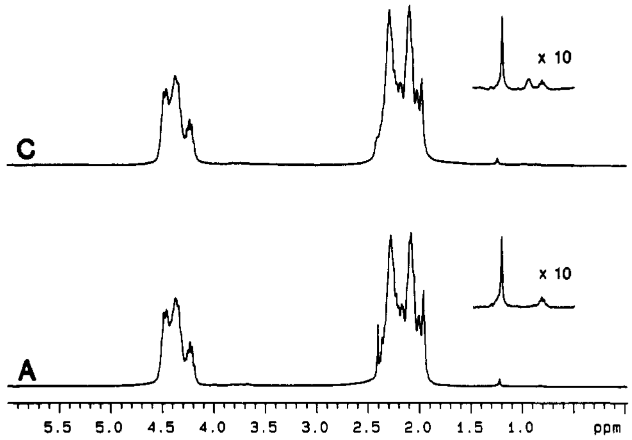


Figure 7. ^{1}H NMR spectra of samples A and C.

unreacted sample (A), indicates that the content of labile structures indeed should be low. The rate is still lower than that expected at zero content according to the extrapolation in Figure 1, even after taking into account the lower values measured today (see above). It must be remembered, however, that shorter sequences due to decreased HCl catalysis is neglected in the extrapolation. As this effect becomes obvious at lower rates, the value of dehydrochlorination at zero content should be still lower. We consider that the degradation rate of sample C is close to that caused by random dehydrochlorination; i.e. sample C should thus contain few labile defects.

The ^{1}H NMR spectra of samples A and C are given in Figure 7. It is of course most interesting to observe any new methyl groups, which should be found around 1 ppm; see magnified part. Sample A has one small resonance (mainly triplet) at 0.8 ppm and a larger one at 1.2 ppm. These can be assigned to the methyl and methylenes, respectively, in the initiator residues (diacetyl peroxydicarbonate was used as initiator). Besides these resonances, sample C has several unresolved resonances between 0.9 and 1.0 ppm. Their intensities are the same also after repeated reprecipitations, and it is therefore plausible that they represent new methyl groups introduced during the reaction with trimethylaluminum.

Integration showed that the content of the new methyl groups in sample C was about 1/1000 monomer units (VC). This is in the same order as the amount of labile chlorine, i.e. tertiary and internal allylic chlorine, in sample A (1.3/1000 VC). It has been observed, however, that nucleophilic substitution of the allylic chlorine in $\sim\sim\sim CH_2CH{=}CH{-}CH_2Cl$ end groups can occur.[47,48] This structure is formed in the mechanism for chain transfer to monomer, and it is the most frequent (0.7–0.8/macromolecule) unsaturated structure in PVC.[49,50] To be able to observe the resonances from this structure more clearly, the acetone-soluble fractions were studied ($M_n \approx 17\,000$). Figure 8a shows parts of the ^{1}H NMR spectra of the fractions obtained from samples A and C. The doublet at 4.05 ppm is assigned to $-CH_2Cl$ in the unsaturated end group.[49] The absence of the doublet in the spectrum of the C fraction indicates that the allylic chlorines have been replaced by methyl groups. This is confirmed by the appearnace of a triplet with correct intensity at 1.05 ppm (Figure 8b), originating from incorporated methyl groups. At the same time the intensity of the signal from olefin protons is the same in the two fractions. This shows that Me_3Al does not initiate polymerization between the double bonds.[51] Thus, terminal allylic chlorines have been substituted with methyl groups:

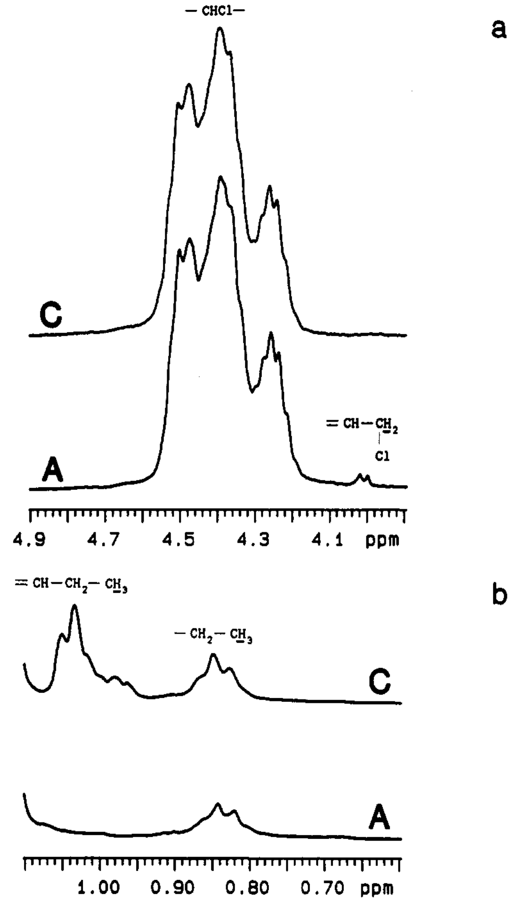
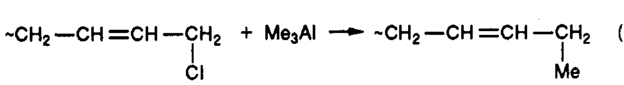


Figure 8. (a) Parts of the ^{1}H NMR spectra of the acetone-soluble fractions from samples A and C. (b) Parts of the ^{1}H NMR spectra of the acetone-soluble fractions from samples A and C.



$$\sim CH_2{-}CH{=}CH{-}\underset{Cl}{\underset{|}{C}H_2} + Me_3Al \longrightarrow \sim CH_2{-}CH{=}CH{-}\underset{Me}{\underset{|}{C}H_2} \quad (9)$$

It is therefore reasonable to assume that also internal allylic chlorines have been substituted. The latter might even show higher reactivity in parallel to their thermal behavior. While internal allylic chlorines are labile, the unsaturated end group has been shown to be stable at the temperatures in question.[50] It is however not possible to obtain a definite proof of substitution of internal allylic chlorine.

To determine the effect of Me_3Al on tertiary chlorine, samples A and C were analyzed with ^{13}C NMR after reductive dechlorination with Bu_3SnH as reducing agent. The spectrum of sample A (Figure 9) shows resonances from methyl, ethyl, butyl, and long-chain branches.[4,39] The content of the different branches is given in Table IV. Earlier investigations on the chlorine substitution pattern in nonreduced PVC samples indicated that tertiary chlorine, which is thermally labile, is associated with ethyl, butyl, and a major part of the long-chain branches.[4,39,52] The total content of these branches is 1.3/1000 VC. In the spectrum of the reduced sample C, which previously had been treated with Me_3Al, the peaks related to branches with tertiary chlorine had been drastically reduced. This is illustrated in Figure 10 for some of the peaks. It can be estimated that sample C still contains ca. 0.1 tertiary chlorine/1000 VC. Starnes et al., recently, showed that most of ethyl branches have tertiary hydrogen atoms.[53] If Starnes et al. results are correct, the concentration of tertiary chlorine is overestimated in the present work. However, this will not affect the conclusions discussed in the present work.

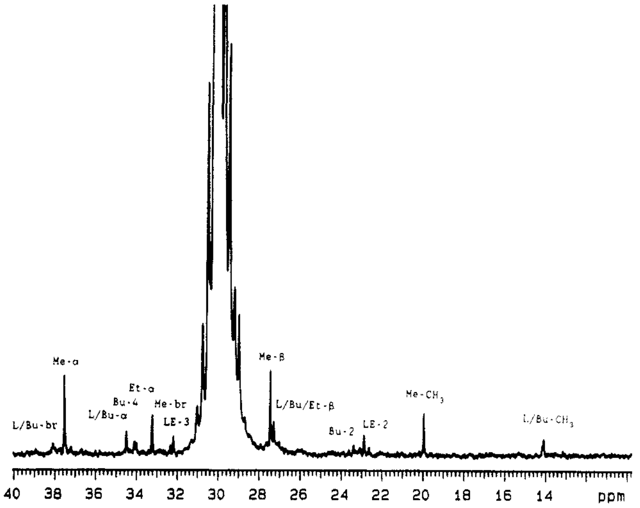


Figure 9. Proton-decoupled ^{13}C NMR spectrum of sample A reduced with Bu_3SnH.

Table IV
Content of Branches in the Reduced PVC Samples

sample	branches/1000 VC			
	methyl	ethyl	butyl	long
A	3.0	0.30	0.87	0.1[a]
C	3.0	0.1[a]		

[a] Uncertain value.

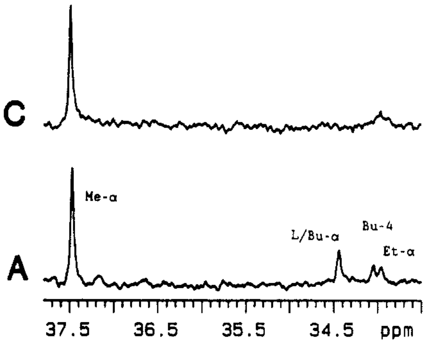


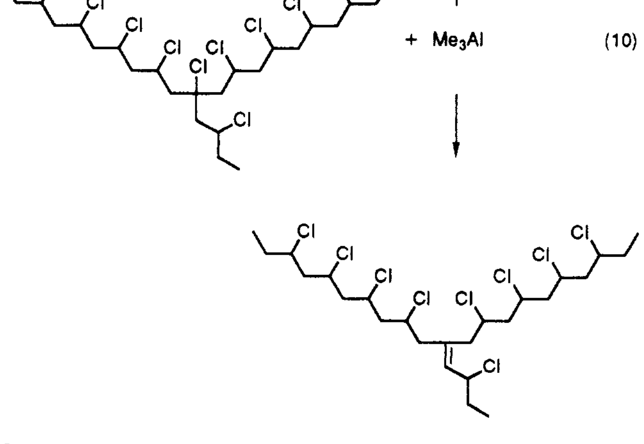
Figure 10. Parts of the proton-decoupled ^{13}C NMR spectra of samples A and C reduced with Bu_3SnH.

It may thus be concluded that the treatment with Me_3Al to a large extent has removed the structures we believe to be the most labile ones, tertiary chlorine and internal allylic chlorine. It should also be emphasized that the total degree of substitution is quite low, on the order of 0.1 mol %. This indicates that substitution of secondary chlorine, which would create terminating sites for zipping dehydrochlorination, is very limited if it occurs at all. The degree of substitution is also considerably lower than the content of GTTG$^-$ triads, which Millan and co-workers claim to be responsible for the instability of PVC. For a polymer obtained at the same polymerization temperature as sample C, their data indicate ca. 0.5 mol % GTTG$^-$ triads.[45,46,54] It is further important to note that the maximal improvement obtained by substitution with sodium benzenethiolate also occurs at a relatively high level of substitution.[46] We therefore consider that the very low rate of dehydrochlorination of sample C, ca. 20% of that of sample A, and the findings about the changes of the structure discussed above, clearly support our view that defects with labile chlorine, in particular tertiary chlorine, strongly influence thermal degradation of PVC.

Similar to the case with the $\sim\sim\sim CH{=}CH{-}CH_2Cl$ end groups, one would expect that tertiary chlorine was substituted with methyl groups during the treatment with Me_3Al; see reaction 3. Miller[51] and Kennedy et al.[55] have reported that substitution does take place in the case of low molecular tertiary alkyl halides. If this was a dominating reaction in the case of PVC, the alkylated structure should indeed be possible to detect with ^{13}C NMR after reductive dechlorination, e.g. as a quaternary branch point with one methyl and one butyl branch. It is easy to calculate the expected chemical shifts for this and similar structures. Even after careful NMR analysis we have, however, not been able to find any set of peaks that can be related to the structures expected after reduction with Bu_3SnH.

Another possible mechanism during the reaction with Me_3Al is β-elimination.[51,55] Elimination of tertiary chlorine would per se lead to a decreased content of the labile tertiary chlorine. In order to determine the extent of elimination, the number of internal double bonds was determined by following the change in M_n caused by oxidative cleavage by ozone.[31] The amount of internal unsaturation was found to be less than 0.1/1000 VC in the unreacted PVC (sample A) and 0.4/1000 VC in the PVC reacted with Me_3Al (sample C). It is obvious that PVC undergoes elimination during the treatment with Me_3Al. The allylic chlorine formed will then most probably be substituted with methyl groups similar to the allylic chlorine in the unsaturated end groups.

Elimination could of course occur for both tertiary and secondary chlorine. If secondary chlorine were eliminated and the allylic chlorine formed were subsequently substituted with methyl groups, one would however expect a higher degree of elimination and substitution. It has also been reported earlier that the use of considerably higher concentrations of trialkylaluminum does not lead to increased levels of chlorine elimination.[21] It is thus most likely that elimination occurs at the branch points. Considering the degree of ethyl, butyl, and long branches (1.3/1000 VC) the amount of new internal unsaturations, 0.4/1000 VC, is rather low. There are however several possibilities for the elimination, e.g. for a butyl branch



(10)

Contrary to a double bond in the main chain, oxidative cleavage of a double bond in the branch would not lead to decreased molecular weight. As the butyl branch is the

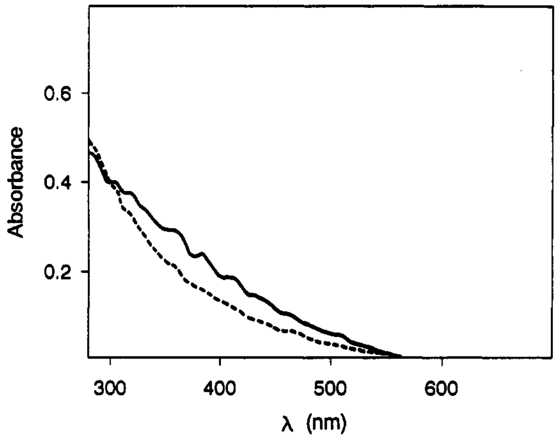
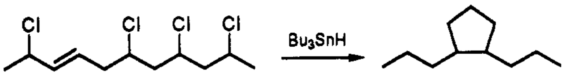


Figure 11. UV–visible spectra for sample C degraded at 190 °C in nitrogen (—) and in HCl (- - -). Both samples were degraded to 0.2% deHCl.

most frequent branch type associated with tertiary chlorine, the number of eliminations detected by ozonolysis would then be reduced already by simple statistics. It may even be that elimination in the branch is favored similar to what has been observed for β-cleavage for tertiary radicals in polyethylene.[56]

If elimination and subsequent substitution take place, it should in principle be possible to observe allylic methyls in the ^{13}C NMR spectra of the reduced samples. It has, however, been shown that unsaturated structures in PVC are rearranged into cyclopentane residues during the reduction with Bu_3SnH,[57] e.g.



(11)

Considering the large number of possible structures which can be formed, the concentration of each structure may be very low. As each structure has its own set of resonances, it is not surprising that we have not been able to observe any of the cyclopentane residues. This would of course be even more pronounced if the tertiary chlorine were partly substituted and partly underwent elimination and subsequent substitution of the allylic chlorine.

It is thus difficult to make any definitive statements about the reactions of tertiary chlorine during the treatment with Me_3Al. The substantial reduction of the dehydrochlorination rate at the low levels of substitution in question is however a strong indication that the tertiary chlorine has been removed without the formation of a new thermally labile structure. Partly, the removal can be due to direct substitution, but most likely to elimination and subsequent substitution of the allylic chlorine.

Sample C is, however, different in another aspect. Surprisingly, it did not show HCl catalysis. A similar result has also been reported by Gupta et al.[21] The degradation rate in the presence of HCl was in fact even lower than without HCl; see Table II. Furthermore, the samples became less discolored, and the polyene sequence distribution was shifted toward shorter lengths; see Figure 11. A possible reason is that aluminum compounds remaining in the polymer after the reaction catalyze readdition of HCl to the double bonds formed by dehydrochlorination. van Hoang et al.[58,59] have reported that other Lewis acids such as organotin chlorides may catalyze such reactions. Analysis showed that the aluminum content of samples A and C is <0.002% and 0.035%, respectively. Studies now under way will provide further information on the effect of low concentrations of aluminum compounds, especially chlorides, on the degradation behavior of PVC.

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