Macromolecules **1988**, *21*, 603–609

ition. These barriers are expected to decrease in a more complete optimization of the transition-state geometries.

The ester phenyl ring in terephthalic PEC has a rotation barrier of 13.1 kcal/mol, as well as a large-amplitude, low-energy oscillation range of ±30° about its equilibrium position. There is no simple or cooperative low-barrier flipping motion for the ester phenyl ring in isophthalic PEC, where the low-energy oscillation or rocking motion range is also much more restricted (±15°).

Comparison of the present results with the results presented in the preceding paper[8] showed that the judicious use of calculations on smaller molecules is a valid procedure. The two sets of results were combined to provide the most complete description of the DMS γ and δ relaxations that could be obtained by considering isolated chain segments. This description is relevant both for the intrachain interactions in the solid polymers and for the dynamical interactions in dilute (up to 10%) solutions of the polymers. In such dilute solutions, intrachain interactions will necessarily dominate over interchain interactions in determining the dynamical processes. By contrast, the relative importance of interchain interactions in the solid polymers is a controversial problem which needs further study.

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Registry No. a, 4824-74-2; b, 10192-62-8; (BPA)(carbonic acid) (copolymer), 25037-45-0; BPA polycarbonate, 24936-68-3; (BPA)(carbonic acid)(isophthalic acid) (copolymer), 31133-79-6; (BPA)(carbonic acid)(terephthalic acid) (copolymer), 31133-78-5; (BPA)(carbonic acid)(terephthalic acid)(isophthalic acid) (copolymer), 31133-80-9.

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Influence of the Dehydrochlorination Rate on the Degradation Mechanism of Poly(vinyl chloride)

T. Hjertberg,* E. Martinsson, and E. Sörvik

Department of Polymer Technology, Chalmers University of Technology, S-412 96 Gothenburg, Sweden. *Received March 17, 1987*

ABSTRACT: The degradation behavior of poly(vinyl chloride) (PVC) samples with considerably increased heat stability has been compared with that of an ordinary suspension PVC. The degradation rate was followed by measuring evolved HCl conductometrically. Structural changes in the polymer were monitored by several techniques: UV–visible spectroscopy was used to follow polyene sequences and GPC to detect changes in the molecular weight distribution and to determine the number of cleavages caused by ozonolysis, i.e., the number of polyene sequences. Besides decreased rate of dehydrochlorination the improved PVC samples become less discolored, i.e., the polyenes are shorter. The results obtained by ozonolysis and UV–visible spectroscopy show that this is not due to an increased frequency of secondary reactions but that a lower number of HCl molecules is evolved from each initiation point. The more severe discoloration, i.e., the longer polyenes, in the normal sample is most likely an effect of higher concentration of free HCl due to the lower initial stability. It is suggested that the polyene propagation, or the "zipper" reaction, is catalyzed by HCl.

Introduction

In thermal degradation of poly(vinyl chloride) (PVC), dehydrochlorination is the dominating reaction and it has been observed already at temperatures just above the glass transition.[1] The stability is thus much lower than could be expected and the reason to the low stability has been the subject of many investigations (see, e.g., ref 2–4). An important question has been the influence of labile chlorine. By using polymers prepared at reduced monomer pressure we have recently been able to correlate the rate of dehydrochlorination to the amount of tertiary chlorine (mainly associated with butyl branches but also with ethyl and long-chain branches) and internal allylic chloride.[5-7] According to our results, the higher content of tertiary chlorine (1–1.5 per 1000 monomer units) compared to internal allylic chlorine (0.1–0.2 per 1000 monomer units) implies that tertiary chlorine is the most important defect even in ordinary PVC. In agreement with other published reports,[2,8-10] we have also found evidence that the normal PVC units are unstable at the temperatures in question, i.e., random initiation will occur.

The dehydrochlorination will lead to conjugated double bonds in the polymer backbone resulting in unacceptable discoloration even at very low degrees of degradation. The maximum length of these polyenes is 20–30[11-13] while the average length is around 10 at low levels of dehydrochlorination.[10,14,15] At higher levels the length decreases according to observations by UV–visible spectroscopy.[14,15] This is the result of secondary reactions, e.g., intra- and intermolecular cyclizations. One observable result of intramolecular cyclizations is the formation of benzene.[16] The intermolecular cyclization will lead to cross-linking

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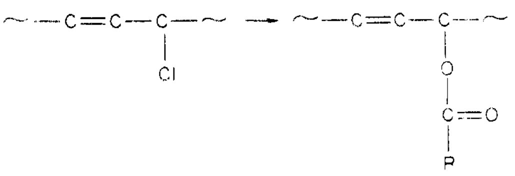
and, accordingly, molecular enlargement can be observed already at 0.3% dehydrochlorination.[14,17] Although Diels–Alder reactions have been proven to be the major reason,[18] other intermolecular reactions leading to enlargement may be operative as well.[19]

A long debated question has been whether HCl has a catalytic effect on the dehydrochlorination (see, e.g., ref 4). Working with HCl-containing atmospheres we have earlier shown that the total rate is indeed increased by the presence of HCl.[17] One reason for the increased rate was that the polyenes became somewhat longer already at low levels of HCl. As higher concentrations had no further effect on the polyene sequence distribution we concluded, however, that catalysis of the random dehydrochlorination was the most important effect of HCl. We could also show that the increased tendency to molecular enlargement in the presence of HCl was solely an effect of the increase in dehydrochlorination rate.

Although many facts are thus known about degradation of PVC, there are still several unanswered questions on the actual mechanism. We have now approached these problems from a somewhat different direction. Utilizing our knowledge about the formation of defects in PVC and their influence on the thermal stability, we have for some time tried to obtain more heat stable PVC by routes that should be more realistic than those reported in the literature.[8,20–30] Besides a decreased rate of dehydrochlorination it has become apparent, however, that PVC with increased heat stability shows another behavior during degradation with respect to polyene sequence distribution and secondary reactions. In this paper, we will mainly discuss the influence of heat stability on the polyene sequence length and the molecular enlarging.

PVC Samples. Three types of PVC have been used in this investigation. Samples A and B were obtained by suspension polymerization at 56 °C in a 5-L stainless steel reactor. Poly(vinyl alcohol) was used as suspending agent and diacetyl peroxydicarbonate as initiator. Vinyl chloride of polymerization grade was kindly supplied by Norsk Hydro Plast AB, Sweden. After water had been charged, air was removed by five cycles of evacuation and purging with extra pure nitrogen (<2 ppm of O_2). All additions were made under a nitrogen blanket. In the polymerization of sample B a small amount (0.1%) of dibutyl tin ester was added to the vinyl chloride before the polymerization according to ref 31 and 32, in order to substitute labile chloride. The following transformation might therefore have occurred:



$$\sim{-}\mathrm{C{=}C{-}C}(\mathrm{Cl}){-}\sim \;\longrightarrow\; \sim{-}\mathrm{C{=}C{-}C}(\mathrm{O{-}C({=}O){-}R}){-}\sim \qquad (1)$$

Sample C, generously supplied by AKZO, Holland, was polymerized with butyllithium as initiator, essentially according to Kolinsky and his co-workers.[20–22] Molecular weight data determined by GPC and viscometry are given in Table I for all samples.

Thermal Degradation. The degradation experiments were performed in a specially designed apparatus described earlier.[33] Bulk samples (150 mg) were heated at 190 °C in nitrogen atmosphere (<5 ppm of O_2). The dehydrochlorination was followed conductometrically and the rate is expressed as evolved HCl in percent of the theoretical amount per minute.

Molecular Weight Distribution. Gel chromatography (GPC) and viscometry were used to determine the molecular weight distribution. Details of the GPC analysis and dissolution procedure have been given earlier.[14] A Waters Associated 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. The setup also contained a SEPEMA on-line viscometer. The viscometer is of the Ubbelohde type and includes a syphon with a volume of 4.57 mL (V_s). The effluent time of pure solvent (t_0) was 113.75 s. The variations in t_0 was less than ±0.01 s. To calculate the intrinsic viscosity ($[\eta]$) eq 2 was used:

Table I
Data for Investigated Polymers

sample	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	$[\eta]$
A	46	109	2.4	0.92
B	46	115	2.5	0.91
C	9.3	163	17	0.65

$$[\eta] = \frac{\sum \Delta t V_s}{t_0 c_0 V_i} \qquad (2)$$

where Δt is the time difference between solution and pure solvent for each fraction, c_0 is the concentration of polymer in the injected solution, and V_i the injected volume.

To calculate MWD and molecular weights averages the computer program devised by Drott and Mendelsson[34] was used, assuming trifunctional branch points. The calibration for linear PVC was obtained via the universal calibration curve as described earlier.[14]

Polyene Sequence Distribution. The polyene 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 by using peroxid-free THF.[14]

Internal Double Bonds. The number of internal double bonds (or sequences) was determined by following the changes in M_n due to oxidative cleavage by ozone of all double bonds. The ozonolysis was performed principally according to Michel et al.[35] 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 ($(\mathrm{C{=}C})_n/1000\mathrm{VC}$) was calculated from the number-average molecular weight before ($M_{n,0}$) and after (M_n) the oxidative treatment:

$$(\mathrm{C{=}C})_n/1000\mathrm{VC} = (1/M_n - 1/M_{n,0}) \times 62500 \qquad (3)$$

Results

The dehydrochlorination experiments were performed at 190 °C in a nitrogen atmosphere and can be related to our earlier results. As can be seen in Figure 1 the three samples exhibited the same general behavior, starting with an apparent induction period followed by an increase in dehydrochlorination rate. To a major part this induction period is caused by the time for the sample to equilibrate thermally and by the dead volume in the system. After about 0.1% HCl loss the plots are linear and the slope is taken as a measure of the stability, see Table II. At somewhat higher levels of dehydrochlorination some small differences can be noted. For the ordinary suspension PVC, sample A, the rate of dehydrochlorination remains constant up to at least 0.8%. In the plots for the improved

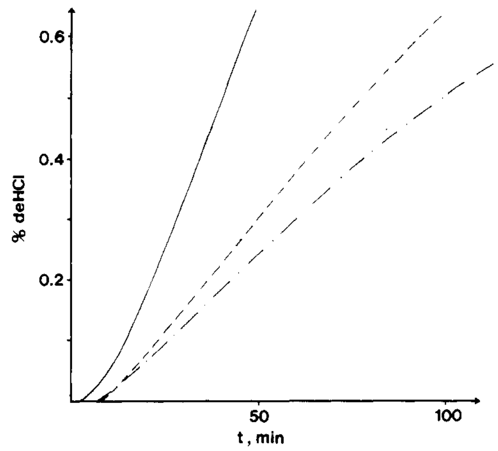


Figure 1. Degree of dehydrochlorination versus degradation time for samples A (—), B (- - -), and C (–•–).

Table II
Dehydrochlorination Rates in Nitrogen at 190 °C

sample	% deHCl/min × 10^3
A	17
B	7.0
C	5.5

PVC samples, on the other hand, a tendency to decreased rate can be seen after 0.4–0.5%.

The dehydrochlorination rate of sample A (17×10^{-3} %/min) is within the range we normally observe for commerical PVC samples. For sample C the anionic mechanism should lead to less defects than the normal radical mechanism. The observed lower rate of dehydrochlorination, ca. 30% compared to sample A, is in agreement with this assumption. We will later report on a detailed determination of the structure of sample C.[36] At present we can state that for a similar PVC obtained from Dr. Kolinsky, we have not been able to detect any ethyl, butyl, or long-chain branches, i.e., defects associated with tertiary chlorine in ordinary PVC. The dehydrochlorination rate at 190 °C measured for the latter sample, ca. 3×10^{-3}%/min, is still lower than that of sample C.

In the preparation of sample B a tin carboxylate was added during polymerization in order to substitute labile chlorine. Compared to that of sample A the dehydrochlorination rate has been reduced to ca. 40%, indicating a much lower content of labile defects. The stability is in fact close to that of the anionic PVC. Similar results have been reported earlier for a number of different pretreatments, e.g., by organotins and/or thiols,[8,23-26] trialkylaluminum,[27-29] and one- to three-carbon alcohols.[30] For sample B physical inclusion of compounds acting as stabilizers during degradation can be excluded since purification by dissolution and precipitation had no effect on the stability. Analyses by NMR further rule out that the stability improvement is caused by major structural changes. Most likely, the decrease in dehydrochlorination rate is an effect of chemical deactivation of labile structures originally formed in the polymer in low concentrations.

Besides the significant stability enhancement, sample B is different compared to sample A in another aspect of great practical interest. For any given level of dehydrochlorination, the discoloration of the former sample is substantially less severe. At, e.g., 0.3% HCl loss the ordinary PVC is brown while the improved PVC is pale yellow. This implies that a larger part of the polyenes in the improved PVC is too short to absorb visible light.

The UV–visible spectra of samples A and B degraded to 0.2 and 0.4% HCl loss are compared in Figure 2. Each maximum has been considered to represent a specific polyene length starting with trienes at 270 nm.[11,37] In a recent paper Braun and Sonderhof[38] have shown that the situation is much more complex. In agreement with the color observation it is, however, obvious that the maximum absorption wavelength corresponds to substantially shorter polyenes in the improved PVC. Especially, it may be noted that the absorption maximum at about 450 nm observed for the ordinary PVC is completely absent in improved PVC.

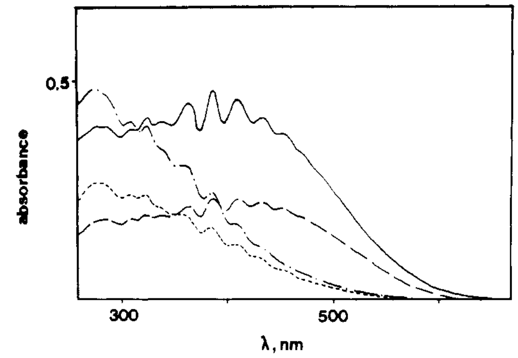


Figure 2. UV–visible spectra for sample A degraded to 0.2% deHCl (– –) and 0.4% de HCl (—) and sample B degraded to 0.2% deHCl (- - -) and 0.4% deHCl (–•–).

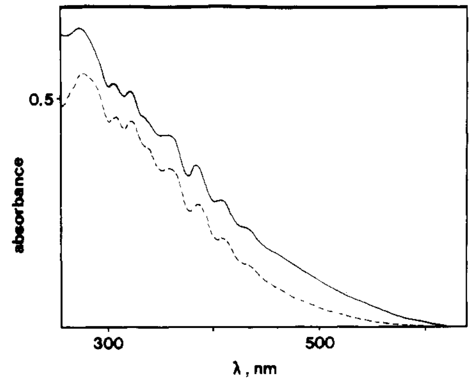


Figure 3. UV–visible spectra for samples B (- - -) and C (—) both degraded to 0.5% deHCl.

A comparison between samples B and C reveals that the polyene sequence distributions of these "stable" PVCs are very similar; see Figure 3. This is a further indication that the improvements observed for sample B mainly are due to the removal of labile structures. It may be noted that shorter polyenes have been reported in several instances in connection with degradation of PVC with enhanced stability.[29,30,39]

As mentioned in the introduction the polyene sequence distribution is shifted toward shorter polyenes with increasing degree of dehydrochlorination due to inter- and intramolecular secondary reactions. The UV–visible spectra in Figures 2 and 3 might therefore not necessarily reflect the distribution of the number of HCl molecules splitted of from each initiation point. To evaluate this point, we also performed ozonolysis, i.e., cleavage of all double bounds by ozone treatment, following the decrease in M_n. As end-positioned unsaturations will have no measureable effect on M_n; eq 3 will give the number of internal scissions. In degraded PVC each polyene sequence will be counted as one scission only.

The molecular weight data and the number of polyene sequences are given in Table III. For any given level of dehydrochlorination it is obvious that the number of polyenes is higher in the improved PVC; see Figure 4. This implies that the number of HCl molecules formed

Table III
Number-Average Molecular Weight before ($M_{n,0}$) and after (M_n) Ozonolysis and the Number of Polyene Sequences, for Samples A and B at Different Degrees of Dehydrochlorination

sample	% deHCl	$M_{n,0} \times 10^{-3}$	$M_n \times 10^{-3}$	$C{=}C_{int}$/1000VC
A	0	46.2	45.3	0.025
	0.3	48.0	41.1	0.22
	0.5	49.0	39.1	0.32
	0.7	50.1	38.6	0.37
	0.9	49.8	36.0	0.48
	1.2	50.8	33.8	0.62
	1.5	50.5	29.6	0.87
B	0	46.0	45.6	0.012
	0.2	50.1	42.3	0.23
	0.3	49.8	40.3	0.30
	0.4	50.4	41.8	0.26
	0.5	51.8	36.9	0.49
	0.6	52.2	39.6	0.38

Table IV
Molecular Weight Averages and Intrinsic Viscosity for Samples A and B Degraded to Different Degrees of Dehydrochlorination

sample	% deHCl	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	[η]
A	0	46.2	109	0.92
	0.3	48.0	114	0.91
	0.5	49.0	113	0.92
	0.7	50.1	182	0.92
	0.9	49.8	219	0.97
	1.2	50.8	331	1.02
	1.5	50.5	567	1.10
B	0	46.0	115	0.91
	0.2	50.1	136	0.91
	0.3	49.8	175	0.98
	0.4	50.4	252	0.98
	0.5	51.8	296	0.99
	0.6	52.2	506	1.11

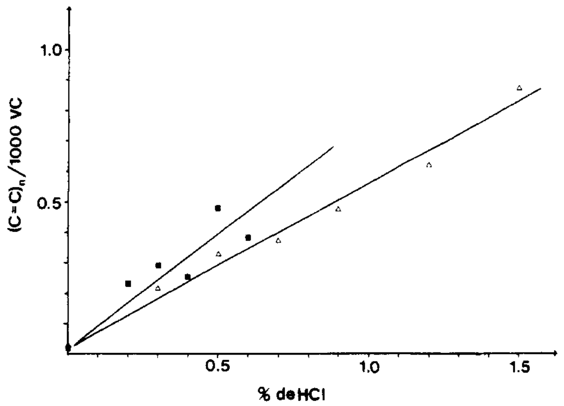


Figure 4. Number of polyene sequences versus degree of dehydrochlorination. Sample A (△) and sample B (■).

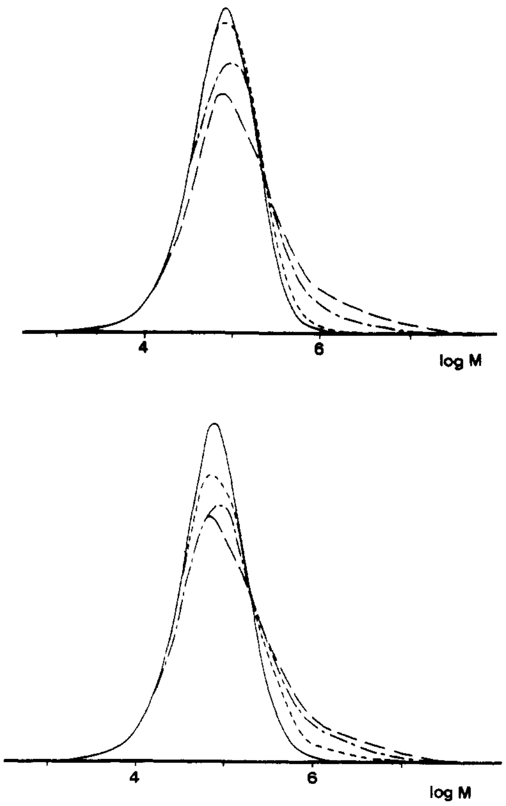


Figure 5. Molecular weight distribution for samples A and B degraded to different degrees of dehydrochlorination. Above, sample A, virgin sample (—), 0.5% deHCl (- - -), 0.9% deHCl (–·–), 1.5% deHCl (– –). Below, sample B, virgin sample (—), 0.3% deHCl (- - -), 0.5% deHCl (–·–), 0.6% deHCl (– –).

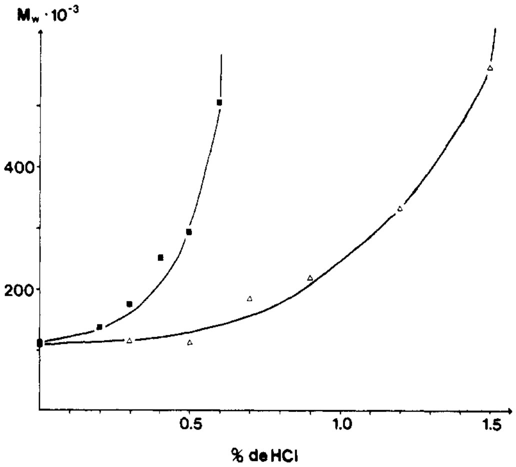


Figure 6. Weight-average molecular weight versus degree of dehydrochlorination for samples A (△) and B (■).

from each initiation point is lower, i.e., in agreement with the UV–visible spectra.

Besides discoloration, cross-linking is an important and disadvantageous secondary effect of PVC degradation. Molecular enlargement can be seen on a rather early stage as illustrated by the changes in the MWD of samples A and B in Figure 5 as well as by molecular weight averages and viscosity values given in Table IV. It looks like the tendency to cross-link should be much more pronounced for the improved PVC when the two samples are compared at the same HCl loss; see Figure 6. Obviously, this must be considered as a negative effect of the improvement. It must be remembered, however, that the time to reach a given degree of dehydrochlorination is much longer for the improved PVC.

Discussion

A decrease in the content of labile structures is expected to increase the stability of PVC, similar to what is observed for samples B and C. A completely stable PVC is, however, not possible to obtain as random dehydrochlorination occurs under the conditions used for processing and stability testing.[2,7-10] In this way new initiation sites are created. In a very recent paper Shapiro et al.[39] discussed in more detail the effect of deactivation of labile structures using alkylthiol/alkyltin mercaptide/alkyltin chloride. The difference in dehydrochlorination rate between the original reference sample and the improved PVC was very similar to that discussed in the present paper. Quite surprisingly it was found that the activation energy was decreased by the chemical pretreatment. The stability

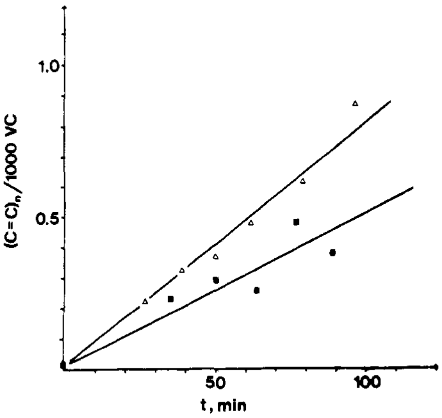


Figure 7. Number of polyene sequences versus degradation time for samples A (△) and B (■).

improvements could instead be ascribed to decreases in the preexponential factor. A reduced content of labile structures was considered to be important in this respect (a). Other contributing factors were considered as well: (b) decreased formation of new initiating structures during degradation and (c) a decrease in the number of HCl molecules liberated per starting site. At present we have only data from degradations at a single temperature, but most likely we should find similar changes in the activation parameters as observed by Shapiro et al.

The data given in Table III and Figure 4 might be used to obtain a rough estimate of the relative importance of the three alternatives, (a)–(c), given above. The difference in average length of the polyenes is readily calculated from the numbers of sequences at the same deHCl loss. It turns out that the sequence length in the improved PVC is about 65% of that in the normal PVC. This might seem not to be too impressive considering the drastic change in the UV–visible spectra. It must be remembered, however, that the extinction coefficient increases with the length, thus emphasizing longer sequences. If the number of polyenes are plotted against time instead, Figure 7 is obtained. Obviously, the rate of formation of new sequences is lower in the improved PVC, i.e., ca. 65% of that in the normal PVC. This can be explained by either removal of labile sites, e.g. tertiary chlorine, decreased rate of random dehydrochlorination, or most likely, a combination of both factors.

This indicates that the two factors (a) and (b) together are of equal importance to (c) alone. The reduced polyene sequence length, and accompanying decrease in discoloration, is, on the other hand, of great potential practical significance. Interestingly, parallell behavior has been reported after several different treatments aimed to destroy labile sites, e.g., by using alkylaluminums[29] or thiol/alkyltin mercaptide/alkyltin chloride.[39] In a series of papers, Millan and his co-workers[13,40–43] have studied the reaction of PVC with a nucleophile, sodium thiophenate. At low temperature, i.e., –30 °C, at least two well-separated stages were observed.[43] In the first part a small fraction of the polymer, between 0.2 and 0.7 mol %, depending on polymerization temperature, reacted extremely fast. Thereafter, the rate decreased to a much lower and constant value, similar for all polymers. For polymers modified to a level corresponding to the fast reaction, decreased dehydrochlorination rate as well as shorter polyenes were observed.[13,42] The changes in the UV–visible spectra were in fact very similar to those in Figure 2.

Table V
Comparison between the Amount of Fast Substitution with Thiophenate[43] and the Expected Amount of Labile Chlorine

t,[a] °C	reactive chlorine per 1000VC				reacted in 1st period per 1000VC
	Cl_T	Cl_A	I[b]	total	
90	2.4	0.1	2.9	5.4	6.3
60	1.3	0.2	1.6	3.1	4.9
0	0–0.5	0.4	0.6	1–1.5	1.5

[a] Polymerization temperature. [b] Structure formula, see text.

It was also observed that the degree of substitution during the fast period increased with polymerization temperature, i.e., with increasing degree of isotacticity among other things. Millan and co-workers[40–44] have therefore strongly argued that a certain isotactic triad, the GTTG* conformation, should react in the fast period and, furthermore, that this conformation should be thermally labile and have a pronounced influence on the instability of PVC. It was also argued that this conformation acted as nuclei for somewhat longer polyenes responsible for the absorption around 450 nm. The shorter polyenes observed after substitution were assumed to be due to selective reaction with this conformation. Although the eventual contribution of defects, such as tertiary and internal allylic chlorine, to the fast reaction was considered, their influence was assumed to be minor.[43] In nucleophilic substitutions, however, the allylic chlorine in $\sim CH_2CH{=}CHCH_2Cl$ (I), which is formed during chain transfer to monomer,[45,46] must be taken into account as well. This structure is thermally stable,[45] but substitution with phenol and nitrate[48] as well as thioltriazine[49] has been observed. The content of this structure can be assumed to be one per macromolecule.[45,47]

The polymers studied by Millan and co-workers were prepared at 0, 60, and 90 °C. An estimation of the amount of tertiary and internal allylic chlorine in the two latter can easily be obtained from published data.[7,50] No reliable data exist for 0 °C polymers but extrapolation of the trends we have observed for polymers obtained in the interval 45–80 °C might serve as an approximation. The estimated concentrations of defects expected to react with thiophenate are given in Table V, together with the degree of substitution in the fast period according to ref 43. Although the former values are somewhat lower, the similarity in the trends is obvious. We therefore consider it more likely that the fast reaction period is more associated with these defects than a specific conformation of isotactic triads. Consequently, the stability improvements observed by Millan and co-workers should be related to removal of labile sites in their conventional meaning.

Another indirect proof of the importance of the labile defects compared with the stereostructure is the behavior of anionic PVC. This polymer has not passed a process aimed to deactivate labile structures, which per se could include certain conformations. Instead, the reduced probability of side reaction in anionic polymerization has resulted in a decreased content of at least tertiary chlorine and, accordingly, increased stability. It is further important to again stress the fact that all slowly decomposing PVC also develop significantly shorter polyenes compared to ordinary PVC. The improved stability may have been reached in different ways and the structure may differ considerably, but the low rate of dehydrochlorination is an obvious common factor. Consequently, the concentration of free HCl on a molecular level should be lower during degradation compared to the situation in ordinary PVC. Considering our earlier investigation on HCl catalysis,[17] it is likely that the reduced discoloration of improved PVC can be related to the lower stationary concentration of HCl. A similar conclusion was recently reached by Shapiro et al.[39]

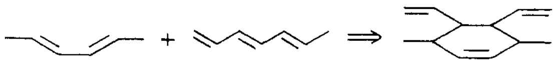
Several different possibilities for HCl to affect the polyene sequence length may be considered. Owen et al.[51] have suggested that migration along the chain can be induced by acid, thus bringing sequences together:

$$-(CH{=}CH)_n- - - -(CH{=}CH)_m- \xrightarrow{HCl} -(CH{=}CH)_{n+m}- \quad (4)$$

The differences in polyene sequence distribution between normal and improved PVC demonstrated in Figure 2 are, however, observed well below 0.1% HCl loss. At this low extent of degradation a mean sequence length of 10 implies that, on an average, only 1 out of 10 macromolecules contains a polyene. Lengthening due to HCl-catalyzed migration is therefore not a probable mechanism to explain the longer sequences observed in normal PVC.

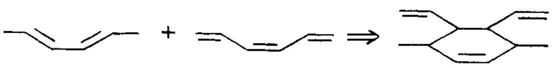
It is more attractive to assume that increased concentration of HCl increases the rate of the polyene sequence elongation relative to the rate of reactions halting the elongation or in any other way reduce the sequence length. If, e.g., HCl inhibits polyene shortening the sequence length will increase with HCl concentration. In their paper Shapiro et al.[39] considered two alternatives: (a) reactions that breaks the conjugation and convert a sequence into two shorter ones and (b) reactions that occur at the growing end of a sequence and stop further elongation.

As mentioned earlier, it has been observed that the sequence distribution is shifted to shorter lengths with increasing conversion due to secondary reactions. Intermolecular reactions leading to cross-links are one possibility. The major part of these reactions have been shown to occur by a Diels–Alder mechanism,[18] leading to cyclohexene moieties in the polymer. The reacting triene may have different configurations, e.g., all-trans or trans-cis-trans:



(5a)

or



(5b)

It has been suggested that acids may prevent the formation of cis double bounds or catalyze their isomerization into the trans configuration.[52] If reaction 5b is markedly faster than (5a), the lower concentration of HCl in improved PVC would thus favor intermolecular cyclization, thus offering a possible explanation of the reduced discoloration. Consequently, the improved PVC should cross-link faster, which seems to be in agreement with the changes in M_w given in Figure 6. For the improved PVC M_w goes to infinity, i.e., gel formation occurs, at about 0.6–0.7% HCl loss, while 1.5% is needed for the normal PVC. This is obviously at variance with our earlier investigation on HCl catalysis.[17] For HCl concentrations in the interval 0–40%, we instead observed that the extent of molecular enlargement was influenced by the degree of dehydrochlorination only. It must be remembered, however, that the number of polyene sequences is much larger in the improved PVC at any given level of dehydrochlorination (see Figure 4), which by itself should increase the tendency to cross-link.

If the changes in M_w are plotted against the degradation time instead, see Figure 8, it is obvious that the rate of molecular enlargement is the same for both samples. Such a behavior would be expected if the cross-linking reaction is slow compared to formation of polyene sequence. A more detailed investigation on the effect of HCl on molecular enlargement will be presented later. At present it is enough to say that an eventual influence of HCl on reactions 5a and 5b cannot explain the differences in polyene sequence distributions between normal and improved PVC.

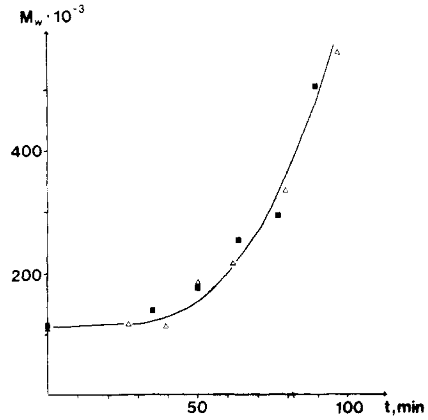
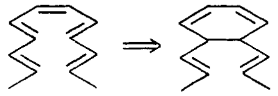


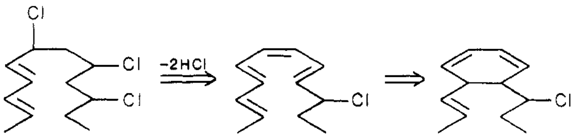
Figure 8. Weight-average molecular weight versus degradation time for samples A (△) and B (■).

Intramolecular cyclizations are believed to be the major reason for the shortening of the polyenes at higher levels of dehydrochlorination.[14,15] The presence of a cis double bond is a prerequisite for cyclization to occur:



(6)

If decreased concentrations of HCl would increase the fraction of cis double bonds as discussed above, reaction 6 should be more frequent in improved PVC. Compared to a situation where (6) does not occur at all, the amount of HCl liberated in each original sequence should stay constant. According to Figure 4, however, the number of sequences is clearly higher for the improved PVC at any level of dehydrochlorination; i.e., the polyenes must have been shorter even without the influence of eventual cyclizations. If the cyclization instead occured at the growing end of a sequence as soon as a trans-cis-trans segment was formed, HCl inhibition according to the discussion above could be operative without being contradictory to the results in Figure 4. In this way the elongation itself should be stopped by removing the allyl activation of the adjacent chlorine. The data presented by Nagy et al. in ref. 53 indicate, however, that reaction 7 is less probable. They followed the changes in the polyene sequence distribution by UV–visible spectroscopy as a function of time for degradations in vacuum. If the removal of HCl by freezing out was discontinued after some time, thus allowing HCl to be accumulated, an almost momentary increase in the average length was observed. To explain the sudden change it must be assumed that not only the few new sequences but a major part of the old ones as well must have become longer at the discontinuation of the HCl removal. Obviously HCl must have reactivated old "dead" polyenes. In this context it should be noticed that in the case of methyl-substituted hexatriene the equilibrium lies almost completely in favor of the cyclic form.[54] Further-



(7)

more, as this electrolytic reaction is symmetry allowed, it should have a low activation energy, and reaction 7, or its retro form, should not be influenced by the polarity of the medium or by catalysts. The above-mentioned observations therefore disqualify reaction 7 to be a major factor controlling the polyene sequence length.

Consequently, the information at hand does not support increased rate of polyene shortening at decreased HCl concentrations as an explanation for the reduced discoloration observed for PVC with enhanced stability. It is thus more likely that low concentrations of HCl reduce the elongation:shortening rate ratio by decreasing the rate of the polyene propagation reaction, i.e., the "zipper" reaction. This is in agreement with our earlier statment.[17] The high probability of acceleration of this reaction by electrophilic acid catalysts has been suggested by other as well.[52] We have compared the degradation behavior of normal and improved PVC in atmospheres containing deliberately added HCl. The results support the view that HCl catalysis of the polyene growth is more important than HCl inhibition of polyene shortening in determining the polyene sequence distribution. These results can be found in ref 55.

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Registry No. PVC, 9002-86-2.

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