RECENT DEVELOPMENTS IN DEGRADATION AND STABILIZATION

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Abstract - In spite of the enormous technical and economical
importance, PVC still offers many open problems due to its
rather low stability against the influence of heat and light.
The present report deals with some recent results from lite-
rature and from the author's laboratory. Discussed are: deve-
lopments in experimental methods for the investigation of the
degradation of PVC; nature and influence of defect structures
in PVC on its thermal stability; mechanisms of non oxidative
and oxidative thermal degradation; photochemical degradation;
reactions between stabilizers and PVC.

1. INTRODUCTION

In spite of the enormous technical and economical importance, PVC still offers
many open problems. Its rather small stability against the influence of heat
and light results in discoloration, HCl-splitting-off and serious corrosion
phenomena, which require stabilization of the polymer for practically all
technical applications.

The very simple basic reaction of PVC is a dehydrochlorination process, from
which many questions arise, most of which are not yet clearified, for example:

Why is PVC so unstable against heat and light, compared to the
much higher stability of low molecular chloroalkanes?

What are the initiation sites of the dehydrochlorination in
the PVC chain?

What are the mechanisms of thermal and photochemical degrada-
tion?

Can the stability of PVC be influenced by the polymerization
process or in any other way?

A better knowledge about the degradation of PVC would be not only of academic
interest but also of practical importance and could help to improve the sta-
bilization either by the development of a more suitable and less unstable
polymer structure or by the introduction of more effective stabilizers.

The open literature contains many recent surveys on the degradation of PVC
(1-7). The present report is therefore confined to some new contributions and
some recent results from the author's laboratory.

2. THERMAL DEGRADATION

2.1. Experimental methods

The industrial investigation of the PVC-degradation usually consists in fol-
lowing the discoloration of PVC-formulations by means of oven- and brabender-
tests.

For scientific purpose the most applied experimental method is the measuring
of the produced hydrogen chloride at a constant temperature (8,9). Recently
the HCL evolution was also determined by degradation at a constant heating

rate (10). Sometimes the degradation in solution has been applied (11,12), but the nature of the solvent may influence the reaction mechanism; therefore, the results of degradation in bulk and in solution can not be compared directly.

The differential thermogravimetry (DTG) represents a supplementary method to investigate the dehydrochlorination process of PVC indicating simultaneously changes in the polymer structure (13,14).

Another important tool for the investigation of degradation processes are the spectra in UV and visible range (15,16), giving semiquantitative information on the average length of polyene sequences and its distribution. Furthermore, ozonolysis of degraded PVC samples provides an insight into mechanism of the dehydrochlorination process revealing the formation of additional unsaturated sites after degradation and permitting the estimation of average polyene sequence lengths (16,17). The evaluation of polyene sequences by Raman spectroscopy has also been reported (18). In some cases IR spectra are also useful to observe changes in the PVC structure during degradation, especially for the study of reactions between PVC and stabilizers (19) revealing exchange reactions of the allylic chlorine atoms with the ester-groups of the stabilizer.

2.2. Initiation of degradation

Most authors agree that normal PVC with head to tail structure should be rather stable against the influence of heat, and be in accordance with investigations of model compounds, e. g. 1, 3, 5 - trichloroheptane (1). Therefore it is generally assumed that structural abnormalities in the polymer chains are responsible for the initiation of the dehydrochlorination.
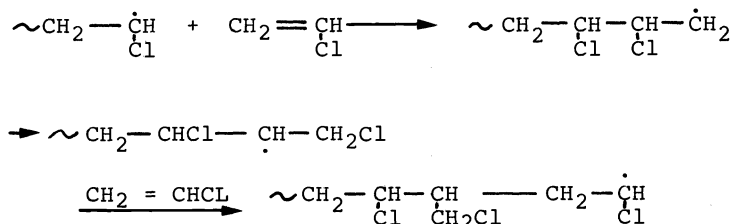
The possible defect structures in PVC are:

> branching
> chloroallyl groups
> end groups
> oxygen containing groups
> head-to-head structures

In addition to these abnormalities the steric order of the monomer units, i.e. the tacticity has some influence on the degradation process.

2.2.1. Branching. A recent review on branching in PVC has been reported by Abbas (20). Many authors used the reductive dechlorination of PVC by LiAlH$_4$ and determined the number of branches by IR spectroscopy.

However, it is now apparent that the extinction coefficient for the methyl deformation is strongly dependent on the length of the side chain to which the terminal methyl group is attached (21). Besides, this reduction has been shown to suffer from several serious disadvantages, including incomplete removal of chlorine and the occurence of various side reactions, e. g. formation of double bonds by HCl abstraction (22) caused by the severe experimental conditions. The reduction with LiAlH$_4$ is therefore an unreliable tool for determining structural anomalies in PVC (23). A much better suited reagent is tri-n-butyl tin hydride, which reacts with alkyl halides RX in a free radical chain reaction (23).

Mainly by the use of C^{13}-NMR it was demonstrated that the short branches in PVC are pendent chloromethyl groups (about 3 per 1000 carbons (24)). It was suggested by Rigo (25) and Park (26) that they may be formed by an intramolecular rearrangement after a head-to-head addition step during the chain propagation. Their formation mechanism, as shown below, was confirmed by C^{13}-NMR spectra of LiAlH$_4$ reduced poly (α-d vinyl chloride) (23):

$$\sim CH_2 - \overset{\cdot}{C}H + CH_2 = \overset{\cdot}{C}H \longrightarrow \sim CH_2 - \underset{Cl}{C}H - \underset{Cl}{C}H - \overset{\cdot}{C}H_2$$

$$\longrightarrow \sim CH_2 - CHCl - \overset{\cdot}{C}H - CH_2Cl$$

$$\xrightarrow{CH_2 = CHCL} \sim CH_2 - \underset{Cl}{C}H - \underset{CH_2Cl}{C}H \longrightarrow CH_2 - \overset{\cdot}{C}H$$

The effect of these chloromethyl branches on the thermal stability of PVC is not yet known but its influence should be dependent on whether the tertiary carbon carries a chlorine or a hydrogen atom.

Model investigations on the influence of chain branches in PVC with tertiary chlorine atoms were made with copolymers of vinyl chloride and 2-chloropropene (27,28). Comparing the dehydrochlorination rates of such copolymers with those of pure PVC prepared under similar conditions, the results indicate the maximum tertiary chlorine content of pure PVC to be 0.1 - 0.2 mol-% (28).

A further possibility to increase branching in PVC, thereby producing polymers of different thermal stabilities and of practical interest, is by the execution of the polymerization under monomer starved conditions (29).

The polymerization of vinyl chloride at subsaturation pressure (U-pol)results in polymer structures different from those which are obtained by normal polymerization. This type of polymerization represents a method to produce PVC with various thermal stabilities, depending mainly on the polymerization conditions. Additionally, U-pol simulates the conditions in ordinary vinyl chloride polymerization after the pressure drop. Sörvik et al. (30) studied the polymerization of vinyl chloride at subsaturation pressure in the presence of different types of seed polymers with monomer and water soluble initiators, respectively. Braun and Holzer (29) studied the polymerization of vinyl chloride at atmospheric pressure with some watersoluble initiators under varying reaction conditions. The changes in structural defects of the resulting polymers were investigated.

The described U-pol can be considered as a type of emulsion polymerization, because a very stable emulsion of PVC-particles is formed.

The applied vinyl chloride pressure changes with increasing polymerization temperature from about 40 % to 10 % of the vinyl chloride vapour pressure, the solubility of vinyl chloride decreases and the radical formation increases; chain transfer reactions are more favoured at higher temperatures resulting in a decrease in average molecular weight with increasing polymerization temperature. The thermal stability of polymers produced at atmospheric pressure is rather low in comparison to ordinary PVC products and even to U-polymers of the Sörvik type.

As the influence of molecular weight on the thermal stability in the investigated range is not substantial, high concentrations of abnormal structures are assumed to be responsible. According to Sörvik (30), polymerization at subsaturation pressure results in products with high degree of long chain branching (LCB) due to an increased probability of chain transfer to polymer and broad molecular weight distribution.

The results are in some agreement with the experiments of Braun and Holzer (29). GPC measurements confirm the presence of a considerable content of low molecular weight material and a broad molecular weight distribution. Apparently, chain transfer to monomer is actually less favoured because of the low monomer accessibility at the reaction site in water. The presence of branch points in PVC, as predicted by the kinetics of transfer to dead polymer during polymerization, has been confirmed in the case of U-PVC by NMR spectroscopy. NMR investigations indicate an unusual high content of branching, being between 1.5 and 7 branches per 100 monomer units.

Chain branching increases proportional to the polymerization temperature and a simultaneous decrease in thermal stability is observed. The 100-MHz-^{1}HNMR-spectrum indicates a signal at δ = 3.75 ppm, which appears as a triplet with a coupling constant of J_{AB} = 6 Hz. According to position and spin-coupling of this signal the following structure is proposed: $Cl-C-CH_2-CH_2-Cl$. Methyl protons, which normally appear at about δ = 0,9 ppm and which would indicate the presence of methyl end groups at branching sites are absent.

2.2.2. Chloroallyl groups. The most discussed initial sites for the thermal dehydrochlorination are allylic chlorine atoms within the PVC chain or at the chain ends. Their number, normally being very small, is determinable both by measuring the allylic chlorine content and by quantitative conversion of the double bonds with specific reagents for olefines.

Frye and Horst (31) as also Bengough and Onozuka (32) substituted the labile chlorine atoms for carboxylates, e. g. cadmium acetate observing changes in the IR spectra.

Further methods consist in a selective scission of the double bonds effecting
reduction in the molecular weight. The most successful reagent for chain
scission is ozone bubbling through a solution of the PVC in 1,1,2,2-tetra-
choroethane maintained at - 20° C (33). Ozonisation of PVC in solid state (34)
or suspended in chloroform (16,35) has also been reported. Generally, chain
scission measurements as detected by reduction in molecular weight take only
into account internal and not terminal unsaturation and do not differentiate
between isolated and conjugated double bonds. The number of unsaturated sites
at the chain ends can be evaluated from the difference between the total and
the internal amount of double bonds. Such values calculated from PVC samples
obtained under varying polymerization conditions differ only within the range
0.6 - 0.8 per chain thus supporting the earlier results of Baum and Wartman
(36).

Normal PVC contains a number of internal double bonds lying in the region of
0.01 per 100 vinyl chloride units (17), however more thermally unstable PVC,
as prepared at reduced monomer concentration, contains about 0.08 (29).

Recently the ozonolytic technique was verified on vinyl chloride/phenyl ace-
tylene (PA) copolymers containing a known number of internal double bonds (17).
Fig. 1 shows the characterization of the vinyl chloride/phenyl acetylene co-
polymers by ozonolytical chain scission of the internal double bonds and by
determination of the incorporated phenyl acetylene units by IR spectroscopy.
Evidently there is a close correlation between the content of phenyl acety-
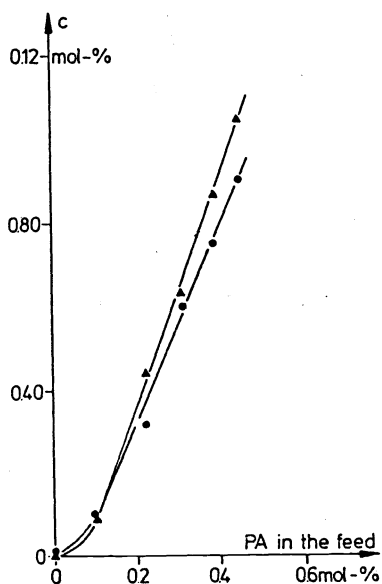lene in the polymer and the number of chain scissions.

Fig. 1. Characterization of the vinyl chloride/phenyl acety-
lene (PA)-copolymers: (●) chain scission number by ozonolysis;
(▲) PA-units in the polymer by IR-spectroscopy

Agreement between the respective copolymer contents of PA, measured by IR
spectroscopy and the number of chain scissions, determined by ozonolysis, con-
firms the selective cleavage of double bonds and therefore the reliability of
the ozonolytic method.

The thermal degradation curves of these VC/PA copolymers(sample 1:0.094,2:0.445
3 : 0.634, 4 : 0.887 and 5 : 1.04 mol-% PA-units in the copolymer) demonstra-
ted in Fig. 2 are remarkably different from those of pure PVC. It is well
known that in the degradation of PVC-homopolymers an induction period is
followed by a steady evolution of hydrogen chloride yielding only about 0.3 -
0.5 % HCl after one hour. VC/PA-copolymers however, as shown in Fig. 2, gave
an enormously increased dehydrochlorination at 180° C. After a fast initial
HCl-evolution to an extent of 10 - 20 %, further propagation of polyene se-

quences seems to be obstructed, suggesting that they have then reached their maximum lenght. From the initial HCl-evolution rates, which increases with the phenyl acetylene content, the activation energy of the decomposition was evaluated to be only 6 - 10 kcal/mole between 100 - 180° C, in contrast to 31 kcal/mole for pure suspension PVC.
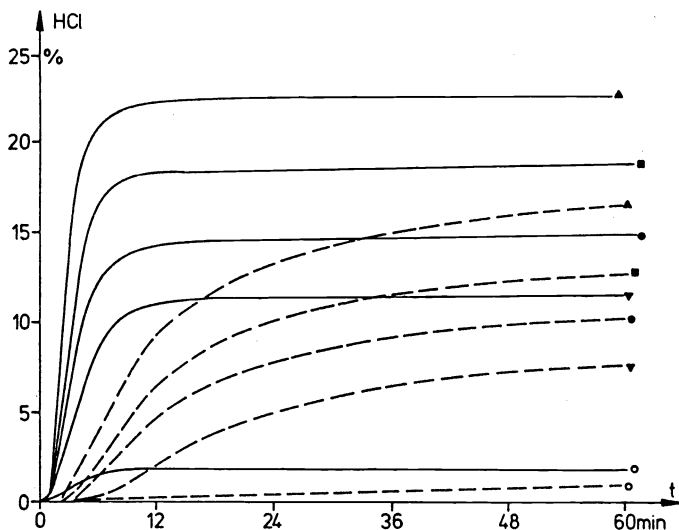

Fig. 2. Dehydrochlorination of vinyl chloride/phenyl acety-
lene (PA)-copolymers in nitrogen stream at 180° C (————) and
at 100° C (-----): sample 1 (○), 2 (▼), 3 (●), 4 (■) and
5 (▲)

Degradation rates of several pure PVC samples prepared under different conditions increase proportionally with their corresponding chain scission numbers. This again illustrates the effect conjugated phenyl groups have in accelerating the rate of degradation caused by the increased lability of the allylic chlorine atoms.
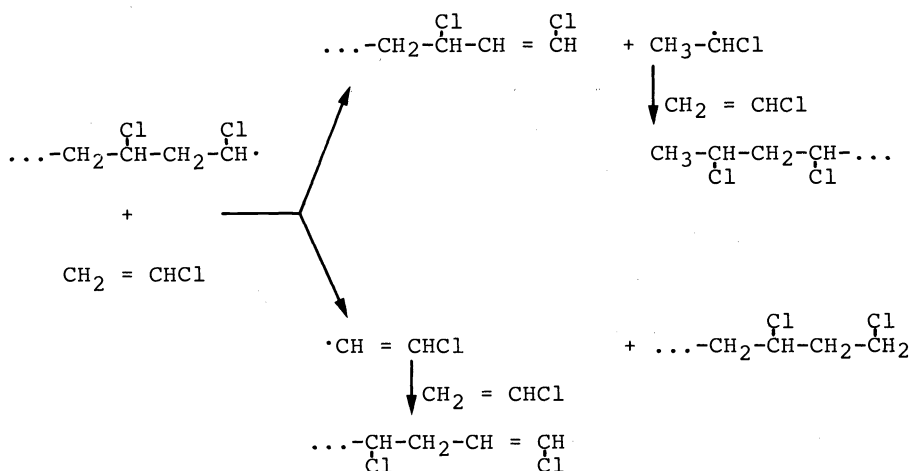
It is generally agreed that the dehydrochlorination process of PVC results in the formation of long conjugated olefinic sequences. Ozonolysis can thus be applied to elucidate the degradation process revealing the creation of additional unsaturated sites in the course of the degradation. After ozonolytic scission the degraded polymers show a lower molecular weight than the corresponding undegraded polymers. Even the bulk-PVC, initially containing no detectable internal double bonds, indicates a respectable decrease in molecular weight disclosing the creation of new internal unsaturated sites during dehydrochlorination.

This could be explained either by a chlorine radical transfer from a propagating polyene, which has started at an unsaturated chain end, to an internal site of the same or another macromolecule or by the presence of further internal initiating sites (37), e. g. tertiary chlorine atoms.

The origin of the internal unsaturation is not completley clarified but in the case of the suspension polymerization of vinyl chloride with azoisobutyronitrile as initiator, it was shown that the amount of hydrogen chloride evolved during polymerization is corresponding with the number of internal double bonds in the polymer (cf. 2.2.4).

2.2.3. End groups. Very recently the discussion about the importance of end groups for the start of the dehydrochlorination became new actuality. Schwenk et al. (45) identified in the methanol soluble low molecular fraction of bulk PVC per molecule 0,5 end groups of the type $- CHCl - CH_2 - CH = CH - CH_2OCH_3$ and 0,25 end groups of the type $- CH_2-CHCl-CH = CH - CH_2Cl$. The remaining ends

consist predominantly in $Cl-CH_2-CHCl$ - and smaller portions of $Cl-CH_2-CH2$ - groups corresponding entirely to results obtained by Pham and Petiaud (39). Possible mechanisms of the formation of chain ends by chain transfer to monomer are discussed by Starnes (40). They can explain the various types of chain ends, some of them may be important as initiation sites for the degradation reaction:

$$...-CH_2-\overset{Cl}{\underset{}{CH}}-CH = \overset{Cl}{\underset{}{CH}} \quad + CH_3-\overset{\cdot}{C}HCl$$

$$\downarrow CH_2 = CHCl$$

$$CH_3-\overset{}{\underset{Cl}{CH}}-CH_2-\overset{}{\underset{Cl}{CH}}-...$$

$$...-CH_2-\overset{Cl}{\underset{}{CH}}-CH_2-\overset{Cl}{\underset{}{CH}}\cdot$$

$$+$$

$$CH_2 = CHCl$$

$$\cdot CH = CHCl \qquad + \ ...-CH_2-\overset{Cl}{\underset{}{CH}}-CH_2-\overset{Cl}{\underset{}{CH}}_2$$

$$\downarrow CH_2 = CHCl$$

$$...-\overset{}{\underset{Cl}{CH}}-CH_2-CH = \overset{}{\underset{Cl}{CH}}$$

Other chain ends arising from transfer reactions to monomer and from propagation steps are:

$$-CH_2-CH = CH-CH_2Cl$$

$$-CH_2-CHCl-CH_2-CHCl-CH2Cl$$

$$-CH_2-CHCl-CH = CH_2$$
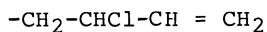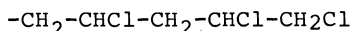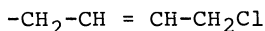
Their importance as initiation sites for the thermal degradation is not yet clear, but at least the allylic end groups may be of similar reactivity as internal unsaturated groups.

2.2.4. <u>Oxygen containing groups</u>. Another possible site of degradation of PVC are oxygen containing groups. Their formation by the polymerization of vinyl chloride in the presence of oxygen was suggested by Bauer and Sabel (41) and discussed by George and Garton (42, 43). Like other vinyl monomers vinyl chloride copolymerizes with oxygen leading during an induction period to alternating polymer peroxides with low molecular weights. These peroxides are not stable and decompose under the polymerization conditions resulting in the main products: hydrogen chloride, formaldehyde and carbon monoxide. The presence of oxygen causes a reduction in final polymer quality (42, 43) but it is not known if this is due to peroxy-, carbonyl or other irregular structures.

In recent investigations attention was focussed on the determination of the concentration of CO, HCl and CH_2O in the course of vinyl chloride/oxygen suspension polymerization. To elucidate the effect of CO, copolymerizations of vinyl chloride with CO were carried out and the products compared with those obtained in the presence of oxygen (44).

Samples of the gas-phase were taken during the copolymerization and analysed by gas chromatography. The variation in oxygen and in CO concentration during the different polymerization stages is shown in Fig. 3. The first stage is marked by the consumption of oxygen copolymerizing to vinyl chloride peroxides and by the simultaneous decomposition of these peroxides producing CO.
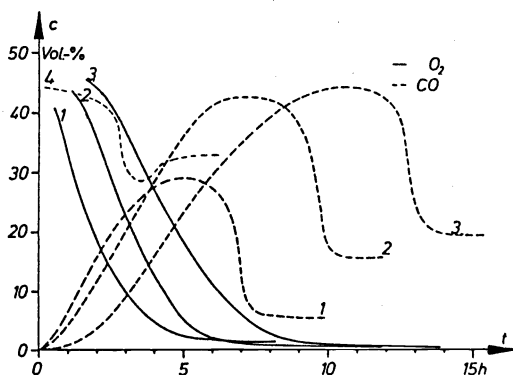
Fig. 3. Oxygen and CO variations in the gas-phase during vinyl chloride/oxygen suspension polymerization (cf. Tab. 1); 1 : 1.77, 2 : 3.43, 3 : 4.75 mol-% O_2 init., 4 : 3.43 mol-% CO init. (= 2 atm)

When oxygen is consumed, in a second stage, vinyl chloride polymerization starts indicated by the formation of PVC particles. CO concentration passes through a maximum. In order to evaluate the conversion of oxygen to CO a polymerization with 3.43 mol-% CO instead of oxygen was performed. The gas-phase contained initially 45 vol-% CO (as shown by plot 4 in Fig. 3) compared to 43 vol-% CO maximum at the polymerization with 3.43 mol-% oxygen.

TABLE 1. Characterization of vinyl chloride/oxygen copolymers

Sample Nr.	O_2 in feed (mol-%)	$\rangle C=O$ in pol. (mol-%)	$\bar{M}_n$	intern. double bonds (mol-%)
12	O	O	53100	0.008
13	0.057	0.048	44900	0.0069
14	0.155	0.080	43400	0.0086
15	0.660	0.093	42200	0.0210
16	1.770	0.228	36400	0.0400
17	3.430	0.230	40000	0.0430
18	4.750	0.260	35450	0.0510

In both polymerization-sets the CO concentration in the gas-phase decreases sharply at the point of the VC pressure-drop suggesting a considerable CO absorption together with VC at the PVC particles. IR-spectra of polymer samples taken in the course of the reaction confirmed that the content of carbonyl groups was not intensified after the pressure-drop.

The development of HCl and CH_2O in the aqueous phase of vinyl chloride polymerizations with different quantities of oxygen is demonstrated in Fig. 4. At total exclusion of oxygen only traces of HCl were detected in the first hours, then during the pressure-drop ("hot spot" stage) the HCl concentration increases followed by a steady low evolution rate.

In several oxygen-free polymerizations of vinyl chloride the amout of HCl evolved was about 0.008 mol-% on PVC corresponding very well to determination of the internal double (44) bonds, which are mainly regarded as initiation sites for the dehydrochlorination. At low oxygen contents (e. g. 0.155 mol-%) HCl and CH_2O evolution are accumulating rapidly up to the equivalent oxygen

amount initially added, comparable to the development of CO in the gas-phase.
In the pressure drop stage the HCl evolution, contrary to the CH_2O formation,
exceeds the oxygen equivalent suggesting a slight thermal dehydrochlorination
of PVC affected by carbonyl groups. However, no direct correlation is evident
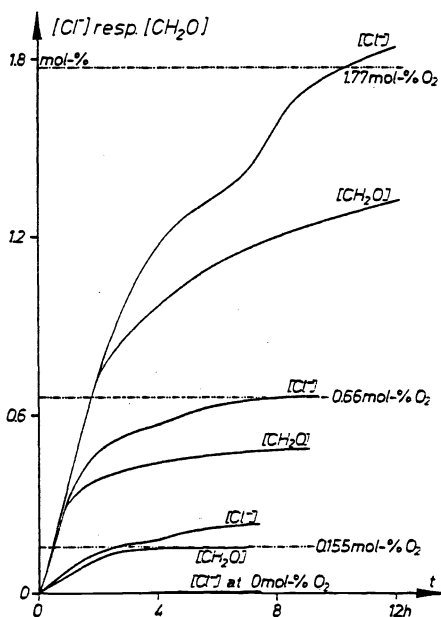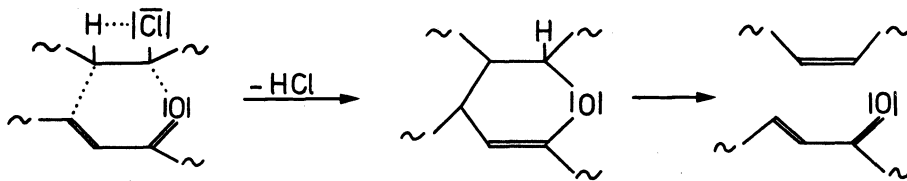to the content of internal double bonds.

Fig. 4. Chloride ion and formaldehyde evolution in the aque-
ous phase during vinyl chloride/oxygen suspension polymeri-
zation

In copolymerizations of vinyl chloride with CO no induction period, a very
low HCl evolution and no change in the polymerization rate was observed. The
content of carbonyl-units in the copolymer was found to be proportional to
the applied CO-pressure and to the initial CO concentration at 50° C in
liquid vinyl chloride determined by gas chromatography. It was evidenced by
reduction of oxygen containing copolymers with $NaBH_4$ that the carbonyl peaks
in the IR-spectra of the copolymers have to be attributed to ketones. The
accuracy of the given carbonyl concentrations(determined by IR-spectroscopy)
was certified by H-NMR studies on vinyl chloride/CO copolymers whose carbonyl-
units were reduced completely to hydroxyl-groups. Internal double bond con-
tents are manifold lower than the corresponding concentrations of carbonyl-
units indicating that the carbonyl groups are almost never conjugated to ad-
jacent double bonds as mentioned by Minsker et al. (45,46).

Thermal degradation tests reveal a close correlation between the dehydrochlo-
rination rate and the number of internal double bonds. Incorporated carbonyl
groups, even at contents up to 2 mol-%, affect only slightly the thermal sta-
bility of PVC. Residual peroxides, however, increase remarkably the initial
dehydrochlorination rate.

A newer contribution to the relationship between structure and stability of
PVC was given by Svetly et al. (47,48). They concluded from kinetic data and
degradation experiments in presence of α,β-unsaturated ketones that the ini-
tiation could not be attributed to labile chlorine atoms in the vicinity of
structural irregularities. They proposed a mechanism, in which the activating
groups of the degradation are represented by oxygen-containing structures.
The constant rate of dehydrochlorination of PVC in an inert atmosphere is
explained as a result of the dynamic equilibrium between simultaneous initi-
ation and termination of the HCl elimination. The active groups are thought
to react with normal PVC units in a cyclic intermediate or a cyclic tran-
sition state:

$$\text{(scheme: H} \cdots |\bar{Cl}| \text{ on cyclohexene ring with } |O| \xrightarrow{-HCl} \text{ H on ring with } |O| \longrightarrow \text{ diene with } |O|)$$

2.2.5. Head-to-head structures.

A first effort to estimate the number of head-to-head-irregularities in PVC was made by Mitani et al. (49) utilizing an iodometric method. In commercial PVC they determined about 0.6 head-to-head structures per 100 monomer units.

Abbas and Sörvik (37) found evidence for the absence of neighbouring methylene groups by C^{13}-NMR spectroscopy. On the other hand, the proposed rearrangement of head-to-head units at the radical chain ends (25,26) resulting in chloromethyl branches would partially explain their consumption during polymerization and thus their absence in the final PVC.

Head-to-head structured PVC can be produced by chlorination of polybutadiene; to obtain a pure head-to-head polymer the chlorination must proceed exclusively by chlorine addition to the double bonds. Crawley and Mc Neill (50) degraded so obtained head-to-head PVC and compared it with commercial PVC. Thermal stabilities of polymers have been investigated by thermal volatilization analysis, thermogravimetry and evolved gas analysis for HCl. The head-to-head polymer has a lower threshold temperature of degradation than normal PVC, but for powder samples it reaches its maximum rate of degradation at a higher temperature. An attempt to explain the breakdown of the head-to-head polymer is made by the same authors. The first steps in the reaction might be the following:

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

$$\downarrow$$

$$\sim CH_2\underset{\underset{+Cl\cdot}{Cl}}{CH}-\overset{\cdot}{CH}-CH_2-CH_2-\underset{Cl}{CH}-\underset{Cl}{CH}-CH_2\sim$$

$$\downarrow$$

$$\sim CH_2-\underset{Cl}{CH}-CH=CH-CH_2-\underset{Cl}{CH}-\underset{Cl}{CH}-CH_2\sim \quad + \; HCl$$

$$\downarrow$$

$$\sim CH_2-\overset{\cdot}{CH}-CH=CH-CH_2-\underset{Cl}{CH}-\underset{Cl}{CH}-CH_2\sim \quad +Cl\cdot$$

$$\downarrow$$

$$\sim CH=CH-CH=CH-CH_2-\underset{Cl}{CH}-\underset{Cl}{CH}-CH_2\sim \quad + \; HCl$$
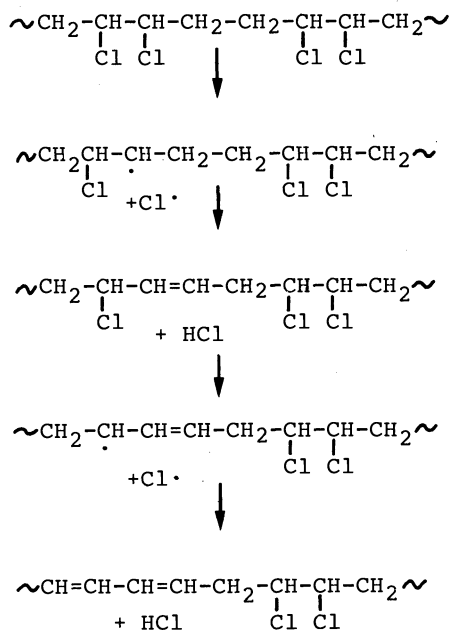
2.2.6. Tacticity.

A problem is also the influence of steric order on the thermal behaviour of PVC. Millan et al. (51,52,53) found, that both the degradation rate and the polyene sequence distribution in degraded PVC depend on the initial tacticity of the polymer. They established that the degradation rate is favoured along syndiotactic sequences, as well as formation of long polyene sequences. The results agree in fractionated and unfractionated polymers, respectively. In order to confirm their results, the same authors studied chemical reactions on degraded PVC such as ozonolysis. The increase of short polyenes relative to the long polyenes with ozonization was found to depend markedly on the content of syndiotactic sequences. In a new and com-

plementary approach Gerrard and Maddams (54) have shown that resonance Raman spectroscopy is a particular useful and sensitive technique for investigating the relative proportions of longer polyene sequences in degraded PVC.

The conclusion of Millan is, that syndiotactic sequences in PVC are less stable than isotactic ones. In contrary to this it is well known that PVC prepared at lower polymerization temperatures is more stable against thermal degradation than PVC prepared at "normal" temperature. But it is also known that the syndiotacticity of low-temperature-PVC is higher than that of normal PVC. Probably this disagreement is connected with the different chemical structure (e. g. in branching, unsaturation etc.) and different physical state of various PVC samples due to various lenghts of tactic sequences being concerned with the cristallization of the polymer. Therefore, the role of tacticity for the thermal degradation of PVC is out of question, but the results are controversial.
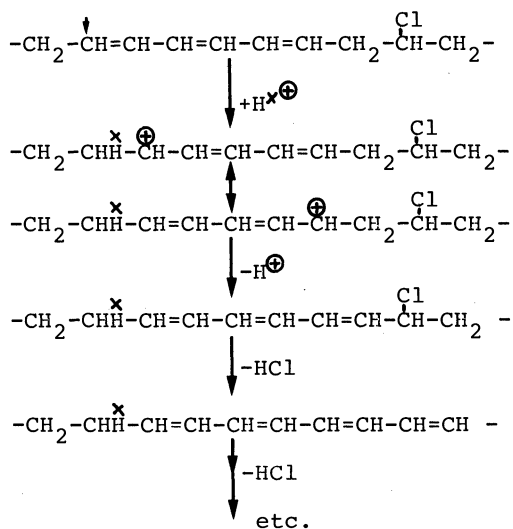
2.3. Mechanism of non-oxidative thermal degradation
The basic processes of the pure thermal degradation are:

1. relatively slow initiation

2. fast allyl activated (zipperlike) propagation
   of the dehydrochlorination by HCl elimination
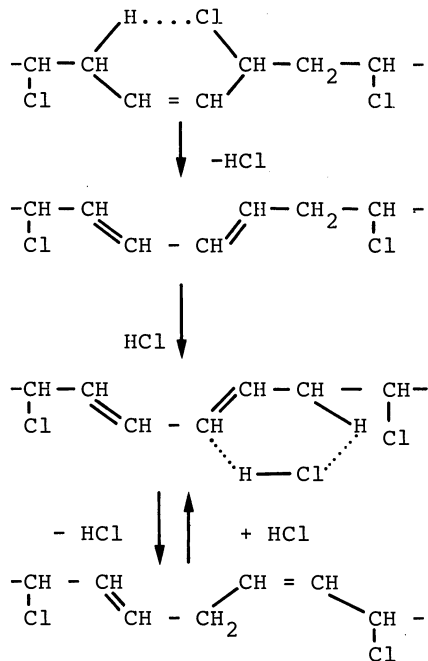   and formation of polyenes

   and

3. termination

The mechanism of these reaction steps is still controversial: in addition to a free radical mechanism ionic and molecular (concerted) mechanisms have also been proposed. Some authors conclude from ESR-studies and experiments with radical traps that free radicals are the intermediates of the pure thermal degradation, both in the presence and absence of oxygen (55). Solvent effects on the rate of HCl loss in solution degradation are, by some authors, discussed as evidence for ionic mechanisms. However, the degradation in phenolic solvents has also been explained by radical reactions (12). Sometimes the autocatalytic effect of HCl is used as a proposition for an ionic mechanism, but there is no direct experimental evidence suggesting that HCl evolution does not proceed via a free radical mechanism. Semiempirical calculations of the transition-state stabilization of the elimination of HCl from model compounds for PVC can explain the experimentally found decrease in the activation energy of dehydrochlorination due to autocatalysis by HCl (56).

It is generally agreed that - at least in bulk - the evolved HCl catalyses further degradation (57). It is known that longer polyenes are formed with HCl catalysis than without. Therefore, the polyenes must play an important role in the catalytic process. Kelen et al. (58) carried out degradation experiments in tritium labelled HCl atmosphere. They found a fast isotope exchange between the polymer and the labelled HCl and proposed the following mechanism involving protonation of polymers (59):

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

$$\downarrow +H^{\ast\oplus}$$

$$-CH_2-CH\overset{\ast}{H}-\overset{\oplus}{C}H-CH=CH-CH=CH-CH_2-\overset{Cl}{\underset{|}{C}}H-CH_2-$$

$$\updownarrow$$

$$-CH_2-CH\overset{\ast}{H}-CH=CH-CH=CH-\overset{\oplus}{C}H-CH_2-\overset{Cl}{\underset{|}{C}}H-CH_2-$$

$$\downarrow -H^{\oplus}$$

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

$$\downarrow -HCl$$

$$-CH_2-CH\overset{\ast}{H}-CH=CH-CH=CH-CH=CH-CH=CH-$$

$$\downarrow -HCl$$

etc.

Recent experiments by J. S. Shapiro (60,61) on the thermal decomposition of solid PVC at low conversion in the presence of HCl or HBr over a temperature range 170 - 210° C also showed the catalytic activity of both hydrogen halides. He proposed an unified mechanism for an overall process consisting of three steps:

1) random generation of a single carbon-carbon double bond in a cis configuration via a radical or unimolecular process

2) 1,4-elimination of HCl via a six-centred transition state yielding a diene

3) hydrogen halide catalysed isomerization of the diene produced in step 2 to regenerate a 1,4-diene structure which can then undergo step 2 repeatedly to form a polyene sequence. Both steps 2 and 3 are molecular reactions:

```
            H....Cl
           /        \
  -CH—CH          CH—CH2—CH -
    |    \       /        |
    Cl    CH = CH         Cl

              |  -HCl
              ↓

  -CH—CH          CH—CH2—CH -
    |    \\      //        |
    Cl    CH - CH          Cl

              |
          HCl ↓

  -CH—CH         /CH—CH — CH—
    |    \\     //          |
    Cl    CH - CH      H   Cl
                  \·.H—Cl.·/

     - HCl  ↓ ↑  + HCl

  -CH - CH        /CH = CH
    |    \\      /          \
    Cl    CH - CH2           CH -
                             |
                             Cl
```

The average length of polyene sequences in thermally degraded PVC is approximately 5 to 10 units (13). By combination of ozonolysis and gelpermeation chromatography it was concluded by Abbas (62,63), that in the early stages of the degradation the number of polyene sequences was constant. After the initial period a very rapid increase in the formation of new initiation sites was observed. This behaviour could be explained either by radical transfer of initiation at new or other labile sites, e. g. tertiary chlorines at long chain branch points. At conversions exceeding about 0,6 % the rate of formation of new polyene sequences gradually decreased and the number of sequences approaches a constant value. This could be explained by a decreasing tendency of radical transfer or by the fact that most of the instable structures are already initiated.

2.4. Thermo-oxidative degradation

Whereas extensive studies on the thermal degradation of PVC in inert atmosphere have been published, thermo-oxidative processes have not received similar detailed attention. The present state of PVC degradation in presence of oxygen is given in a recent report by Tüdös et al. (64,73).

The main effects of oxygen on the thermal degradation of PVC are:

1. The thermal dehydrochlorination of PVC is accelerated by oxygen (at 1 atm by a factor of 2 to 5)

2. Main chain scission during degradation, which is not observed in the absence of oxygen

3. A diminished rate of colour formation;and the absorption spectra of PVC
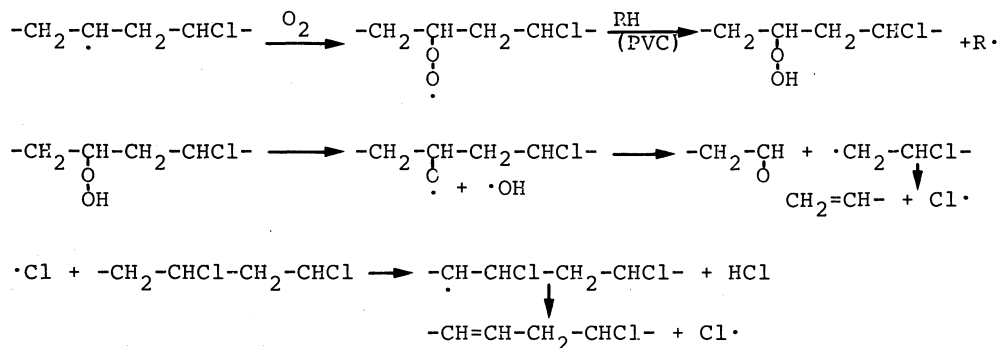   in case of oxidative degradation produces unresolved patterns.

In comparison to virgin PVC the loss of HCl of thermally pretreated PVC is
much faster. Thus polyene oxidation is accompanied by HCl evolution, the rate
of which increases with increasing polyene content and oxygen partial pres-
sure. Quantitative measurements of the oxygen consumption show that not all
oxygen is bond to the polymer; in addition to HCl, other volatile products,
e. g. water, are formed.

The mechanism of the thermo-oxidative degradation of PVC is not known in de-
tail, but the main reaction routes are (64):

1. Primary HCl loss and polyene formation are similar processes in the pre-
   sence and absence of oxygen.

2. The polyene sequences are oxidized in a fast radical reaction

3. The peroxy products formed decompose rapidly

4. The radicals found during the oxidation of polyenes and decomposition of
   peroxides attack intact monomer units and indicate further HCl evolution.

5. Only in the solid state is auto-acceleration of the degradation observed,
   and is therefore not an inherent property of the thermooxidative process.
   This acceleration may be the result of the catalysis by HCl, the removal
   of which in solid state is much slower than in solution.

A practically important conclusion of the mentioned reactions is the fact that
the first step in thermal and thermooxidative degradation is the same; there-
fore the stabilization in both cases must prevent the zipperlike HCl loss.

The complete reaction scheme of the thermo-oxidative degradation of PVC is
not yet known. Gupta and St. Pierre (65) proposed a mechanism, which is based
on the reaction of oxygen with radicals generated in PVC to form unstable
peroxy radicals. In addition, it is proposed that oxygen reacts directly
with conjugated polyenes to form peroxy linkages:

$$-CH_2-\overset{\cdot}{C}H-CH_2-CHCl- \xrightarrow{O_2} -CH_2-\underset{\underset{\cdot}{O}}{\overset{|}{\underset{|}{O}}}{\overset{|}{C}}H-CH_2-CHCl- \xrightarrow[(PVC)]{RH} -CH_2-\underset{\underset{\cdot}{OH}}{\overset{|}{O}}{\overset{|}{C}}H-CH_2-CHCl- +R\cdot$$

$$-CH_2-\underset{\overset{|}{OH}}{\overset{|}{O}}{\overset{|}{C}}H-CH_2-CHCl- \longrightarrow -CH_2-\underset{\overset{|}{\cdot} + \cdot OH}{\overset{|}{O}}{\overset{|}{C}}H-CH_2-CHCl- \longrightarrow -CH_2-\underset{O}{\overset{|}{C}}H + \cdot CH_2-CHCl-$$
$$CH_2=CH- + Cl\cdot$$

$$\cdot Cl + -CH_2-CHCl-CH_2-CHCl \longrightarrow -\overset{\cdot}{C}H-CHCl-CH_2-CHCl- + HCl$$
$$-CH=CH-CH_2-CHCl- + Cl\cdot$$

A similar process is described by Decker (66) for the γ-irradiation of PVC in
presence of oxygen.

2.5. Secondary processes of thermal degradation
Whereas the early steps in the thermal degradation of PVC have been investi-
gated by many authors, the secondary processes at higher degrees of HCl loss
have received only little attention. The main processes are crosslinking, for-
mation of aromatic volatiles, Diels-Alder-reactions and - in presence of oxy-
gen - oxidation of polyenes.

The crosslinking results in an increasing unsoluble part of the polymer with
increasing reaction time; later on the viscosity number of the polymer de-
creases due to chain scission (67). The polyene sequence lenght does not in-
crease remarkably with longer degradation times, probably due to cyclization
of polyenes. With increasing degree of dehydrochlorination, the chain scission
is accompanied by the formation of aromatic compounds, predominantly benzene.

In the presence of oxygen other reactions of the polyenes result in the for-
mation of peroxides and smaller amounts of hydroperoxides. Due to the preoxi-
dation the rate of the thermal dehydrochlorination is increased (64).

The rate of crosslinking depends (68) on the amount of keto allyl groups in
the chains:

```
-C-CH=CH-CH-
 ‖        |
 O        Cl
```
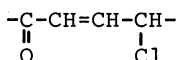
At higher temperatures (550° C) conjugated aromatic pyrolyzates like benzene,
styrene, naphthalene, biphenyl and anthracene are formed via intramolecular
cyclization. Mixed aromatic-aliphatic pyrolyzates (toluene, indence, methyl-
naphthalene) are formed at least partially via intermolecular (crosslinking
and hydrogen transfer) processes (69). The formation of traces of vinyl chlo-
ride during the processing of PVC at 210° C is described by Wakeman and John-
son (70). Rabek et al. (71) investigated the oxidation of polyenes in PVC by
molecular and singlet oxygen. They discussed, similar to others (72), the
formation of six- or five-membered cyclic peroxides during the thermal oxi-
dation of polyenes in PVC by molecular oxygen:
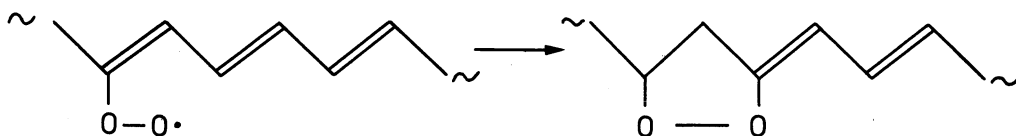
3. LIGHT INDUCED DEGRADATION

The instability of PVC against light is as long known as its thermal instabi-
lity, but compared to the thermal degradation much more questions are still
open. The number of published papers on the fundamentals of photodegradation
of PVC is much smaller than on practical problems of aging of PVC in presence
of light and air (see (83)). At least partly, due to the different experimen-
tal conditions used, results published in literature are very often contro-
versial. Therefore, the first necessity seems to make a carefull study of
the various factors influencing the experimental data. Most authors deter-
mined the discolouration of the samples in presence of light and/or oxygen
and in only rather few investigations the HCl-splitting off was determined
simultaneously. For practical purposes also changes in the mechanical proper-
ties during irradiation were used.

3.1. Recent experimental results

As mentioned, many controversial results in literature are due to different
experimental conditions. Therefore we investigated some factors influencing
the dehydrochlorination and the discolouration of PVC (74): intensity of
light (energy per square and time unit); temperature of the sample; thickness
of the films; partial pressure of oxygen in the degradation atmosphere.

The UV spectra of the polymer after irradiation of PVC to the same degree of
degradation (same HCl amount splitt off) with different light intensity show
less discolouration at higher than at smaller light intensity (75,76). This
can be explained by subsequent crosslinking under participation of the formed
double bonds or polyene sequences. Therefore, no direct correlation between
discolouration and degree of degradation (HCl evolution) can be expected.

It is known, that the rate of HCl elimination during irradiation is decrea-
sing with longer times of irradiation (75,76): in the beginning the rate is
very dependent on the intensity, later on a nearly constant rate is observed.
Probably due to the shielding effect of the formed polyene sequences the in-
tensity of the light inside the sample is decreasing with increasing time
(77).

Also of importance for the rate of degradation is the temperature of the
sample. For the activation energy of the HCl elimination between + 20° C
and + 90° C a value of about 8 kJ · mol^{-1} was found (77) independent from

PVC type and atmosphere. Below 0° C the activation energy increases to 30 to 40 kJ · mol^{-1}, which is probably due to the permeation process of HCl through the polymer. In the presence of oxygen the activation energy of oxidation at room temperature is about 22 kJ. · mol^{-1}, indicating that the photooxidation is much more sensitive to the influence of temperature than the dehydrochlorination. This observation is of importance for the simulation of natural weathering of PVC.

Another important factor is the thickness of the PVC sample. It depends strongly on the intensity of the light how deep the irradiation can penetrate into the film. The solubility of the evolved HCl in PVC causes an "induction period" depending on the film thickness; therefore, HCl which was splitting off from polymer layers below the surface can only be measured in the gas phase after migration through to upper layers of the sample. These effects are the reason why only results obtained with very thin films of known thickness can be compared directly.

It should also be mentioned that films cast from solutions can contain residues of the solvent, which may play a role in the photodegradation of PVC. So Rabek et al. (78) have shown that tetrahydrofuran during UV irradiation in presence of oxygen forms α-hydroperoxy-tetrahydrofuran and oxy-radicals, which participate in the dehydrochlorination of PVC.


3.2.   Mechanism of Photodegradation

The light degradation of PVC is determined by three basic processes: photolysis, photooxidation and dehydrochlorination. These phenomena are rather complex and only clarified to some extent. One of the main unsolved problems concerns the initiation of the photodegradation since pure PVC should not absorb light of wave lenghts above 250 nm. Therefore, hydroperoxides, carbonyl groups and unsaturations have been suggested as possible chromophores responsible for the initiation step. Very recently Decker (79,80) determined precisely the quantum yields of dehydrochlorination, chain scission and crosslinking in the photodegradation of PVC showing the predominant effect of double bonds (see below).

During the photolysis of PVC in a nitrogen atmosphere, dehydrochlorination leads to the formation of polyen sequences. Hydrogen chloride is evolved with an increasing rate during irradiation which is exclusively due to the increased absorption of light by the irradiated polymer. The absorption spectra move towards longer wave lenghts with longer exposure to light, which can be explained by the conversion of short polyene sequences into longer ones (81). The quantum yield (amount of HCl per g PVC evolved to the number of photons absorbed by 1 g of the polymer) is constant throughout the photolysis. From the constant value of the quantum yield Decker (80) concludes that initially present unsaturations are responsible for the initiation step, whereas carbonyl groups and hydroperoxides are not expected to play an important part in the initiation steps. In presence of oxygen intermediately formed tertiary peroxy radicals yield α-chloroalkyl radicals which decompose by ß-scission, either by splitting off a chlorine atom or by C-C cleavage thus increasing the dehydrochlorination and chain scission in the oxidized polymer.

The increase of the UV absorption of the polymer for a given amount of HCl is almost as high for PVC films irradiated in pure oxygen than in nitrogen. Therefore, oxygen cannot have a strong bleaching effect of the polyenes formed during the photolysis and the propagating polyenyl radical -CH=CH-ĊH-CHCl- is too short living to react substantially with oxygen, i. e., the chlorine splitting off competes successfully with the scavenging of oxygen. The major oxidation process is then involving primarily the peroxy radical

-CH=CH-ĊH-CH$_2$-CHCl-   and the α-chloro-peroxy radical   -CH$_2$-C̈(Cl)-CH$_2$-CHCl- formed
         ⅼOO•

by the abstraction of a tertiary hydrogen by peroxy radicals. The chain scission can be explained by formation of hydroperoxides which yield α-chloroalkyl radicals, disappearing by a ß-scission, either by cleavage of C-C bonds or by a chlorine atom:
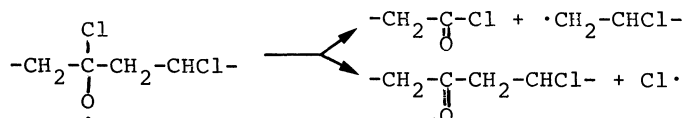
The additional production of propagating chlorine radicals accounts for the enhanced degradation in the presence of oxygen.

The rate of HCl-evolution depends also on the concentration of oxygen in the atmosphere.At least in the initial step of the photoelimination oxygen can inhibit the reaction, as oxygen is a very active triplet quencher (75). With increasing oxygen concentration the rate of oxydation reactions increases and therefore also the rate of dehydrochlorination (82). At high oxygen concentration the oxydation of polyenes causes a consumption of polyenes and a bleaching effect. These results show how complex the photodegradation of PVC is; the simultaneous HCl-elimination and oxydation are strongly dependent from each other and for accelerated aging tests of PVC it is very important to elucidate the relations of both reactions. By no means only from the discolouration conclusions on the degree of degradation or on the mechanism the photolysis of PVC can be drawn.

4. STABILIZATION OF PVC AGAINST HEAT

The rather low stability of PVC against heat requires the stabilization for all technical applications or at least during heat treatment at processing. A large number of various stabilizing systems is known and many of them are used in technical scale. A general survey was recently given by Wirth and Andreas (83).

There are two main functions of all stabilizing systems: First of all the preventive function:

> binding (neutralization) of hydrogen chloride and thus exclusion of its autocatalytic effect

> exchange of labile chlorine atoms and thus elimination of inition sites

> antioxidant effect and thus reduction of formation of inition sites.

The second function is of curative nature:

> Addition of eliminated species from stabilizers to damaged sites like double bonds or polyene sequences

> Destruction of onium complexes to improve the colour.

To fullfill these functions there are three important stabilizing reactions
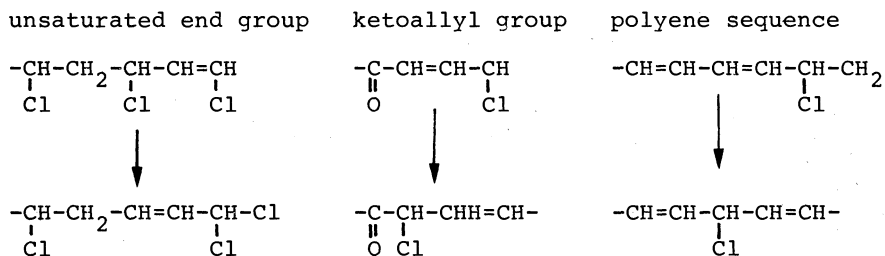
1. Binding of hydrogen chloride

   A classical example is the addition of sodium carbonate or the use of alkaline inorganic substances in the emulsion polymerization of vinyl chloride. Similar is the reaction of split off HCl with epoxides or with calcium stearate. In all these cases the reaction products are inactive and prevent the autocatalytic effect of HCl on the degradation process as well as the formation of coloured onium-complexes by addition of HCl to polymers according to Schlimper (84).

2. Exchange of labile chlorine

   The fundamental research work of Freye et al. has shown that this type of stabilizing reaction is an exchange of e. g. allylic chlorine by organic residues of the stabilizer connected with an allylic rearrangement (85,86, 87)
   Typical examples are barium or cadmium soaps (88) or some organo tin compounds. It is well known that metal chlorides formed during these reactions have an influence on the thermal stability of PVC. Zinc chloride, e. g., has a strong destabilizing effect, whereas lead chloride behaves almost indifferently. A rather unique effect is shown by alkyl tin chlorides which cause a significant retardation of the dehydrochlorination rate of PVC. According to Wirth et al. (89) under certain conditions a chloro allyl isomerization is observed, which explains the stabilizing effect of organo tin chlorides on PVC. This reaction can occur with unsaturated end groups, with keto allyl chloride groups proposed by Minsker et al. (53) as starting species for the dehydrochlorination, or with polyenes:

unsaturated end group   ketoallyl group   polyene sequence

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

$\downarrow$ $\downarrow$ $\downarrow$

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

It should be mentioned that not only metal containing stabilizers are able to give exchange reactions with labile chlorine atoms of PVC but also pure organic compounds like 2-phenylindole or ß-aminocrontonic acid esters (cf 83).

3. Addition of stabilizers or their reaction products to polyene sequences

This reaction is known, e. g., in the case of organo tin mercaptides when the formed mercaptanes are added to double bonds or polyenes in PVC which is an important second reaction for incorporation of sulphur into PVC besices the above mentioned exchange reactions between labile chlorine in PVC and organo tin mercaptide stabilizers.

Other important stabilizers for PVC are antioxidants which can prevent the autooxidation of PVC and the formation of additional initiation sites during processing of PVC in presence of oxygen.

Another problem connected with the stabilization and pigmentation of PVC is the "plate out" effect which is mainly observed during the processing of rigid and semi-rigid PVC by extrusion or calandering. Plate out is a very complex problem, depending from the composition of a PVC compound, the used additives like stabilizers, pigments, fillers and lubricants, but also on the processing conditions like shear rate, temperature etc. In the literature up to now only little information about the composition of plate out and the reasons of its formation can be found (90,91,92). Recently we have started a research project together with the Institut für Kunststoffverarbeitung in Aachen to elucidate relations between composition of PVC compound, processing conditions and nature of plate out (93). We have developed an analytical technique for the separation and quantitative determination of the plate out whereas in Aachen a tool for simulation of plate out effects during extrusion of PVC was built. First results show a strong dependence of the plate out formation and composition on the mass temperature during extrusion. The composition of the plate out of a Barium-Cadmium stabilized PVC with about 4 % TiO_2 shows a remarkable concentration of TiO_2 (about 10 to 40 wt.-%) and insoluble and soluble components from the additives (about 40 to 60 wt.-%), whereas only about 20 - 25 wt.-% PVC are present in the plate out mixture. We hope that future investigations will show some quantitative relationship between the various parameters responsible for the plate out formation during extrusion of PVC.

5. CONCLUSIONS

The presented survey shows that in spite of the enormous effort to elucidate the relations between structure and stability of PVC many questions are still open. The main problem is the little knowledge about the origin of the defect structures in PVC which without doubt are responsible for its instability. At least partially this is due to the small content of such abnormal units in the PVC chain, which offers a lot of problems in analytical determination of these structures. Therefore it seems of great importance to develope more sensitive methods for the quantitative analysis of all possible structural units in PVC. Another task is the further investigation of the relationships between the physical state and morphology of the solid PVC and its thermal behaviour. Finally, the mechanisms of degradation are by no means clarified and require additional experimental work in solid state and in solution. Progress in this respect would also be of importance for the understanding of the reaction between PVC and stabilizers and the development of new stabilizer systems.

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