THERMAL DEGRADATION OF POLYVINYL CHLORIDE

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ABSTRACT

A survey is given of the recent advances in the study of and the present knowledge of the thermal degradation of polyvinyl chloride. The sites for initiation of the thermal degradation, the mechanism of the dehydrochlorination, the discoloration of PVC by heat and the influence of plasticizers on the rate of degradation are discussed.

1. INTRODUCTION

For many years polyvinyl chloride (PVC) has been one of the most important technical polymers. A great disadvantage of PVC is its rather low thermal stability. It is well known that PVC splits off hydrogen chloride at high temperatures; during this process polyene sequences are formed and the polymer is discoloured. Up to about 220° hydrogen chloride is the only volatile degradation product; in the presence of oxygen, in addition to the dehydrochlorination, oxidation reactions can occur, which can also initiate chain scissions. Nowadays it is possible to suppress these undesired degradation reactions by using stabilizers, but the mechanisms of the dehydrochlorination of the PVC remained as obscure as the nature of the initiation sites from which the dehydrochlorination starts. There is also very little known about the reactions between PVC and stabilizers. Due to the fact that the dehydrochlorination of PVC is one of the most important technical reactions with polymers it would be important to have a better understanding of the above mentioned questions.

In recent years several detailed surveys on the degradation of PVC have been published[1–4]. The present paper therefore is confined to the discussion of newer developments and some open problems. The main topic is the thermal degradation; the degradation by radiation or chemical reagents will not be discussed. After a short review of the experimental methods used for the

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investigation of the dehydrochlorination of PVC the following topics will be discussed:

1. Sites for initiation of thermal degradation.
2. Mechanism of dehydrochlorination.
3. Discolouration during degradation.
4. Degradation in the presence of plasticizers.

2. EXPERIMENTAL METHODS

For investigations of the thermal degradation of PVC most authors use measurements of the hydrogen chloride split off. Thus various apparatus have been described in which the HCl is measured, after removal from the polymer sample, by electrical conductivity[5]. In a few cases the change in the electrical conductivity of the solid polymer due to the HCl splitting off[6], or the change in pressure due to the gaseous HCl[7] is used. The potentiometric measurement of the degradation can also be combined with viscosimetric investigations in a Brabender–plastograph[8]. Recently the thermogravimetric analysis of the
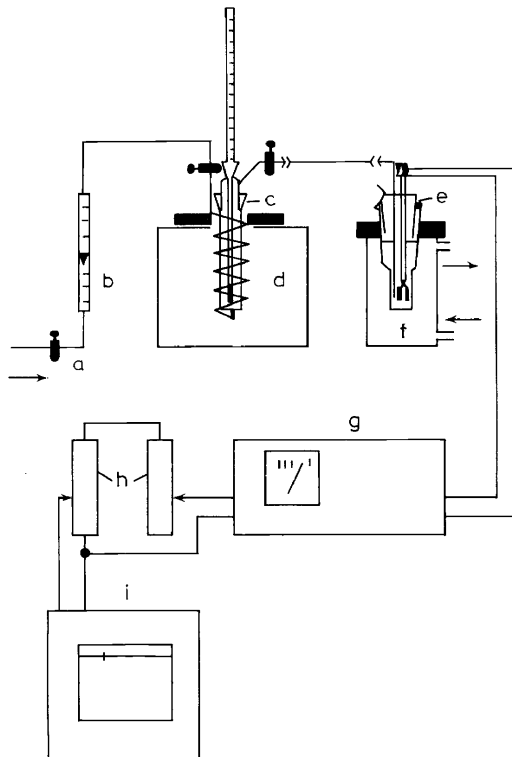

Figure 1. Apparatus for the measurement of the thermal HCl splitting off from PVC (a) valve for regulation of the gas rate; (b) rotameter; (c) vessel for the sample; (d) thermostat; (e) conductivity measurement cell; (f) thermostat for (e); (g) conductivity meter; (h) resistances; (i) recorder.

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polymer, in combination with the potentiometric determination of the HCl[9, 10] and thermal volatilization analysis[11] have also been applied. Another possibility is the photometric determination of the discolouration during the degradation[12].

For practical purposes the discolouration of a PVC compound during processing can be used as a measure of its stability. For basic research this method can be used only in combination with the measurement of the HCl splitting off. Therefore most authors use, for kinetic and mechanistic investigations, the direct determination of HCl; an important factor is the exact constancy of the temperature and the complete transfer of the HCl into the conductivity cell[5]. The potentiometric determination of the HCl split off is possible with high sensitivity, so that the initial part of the reaction (conversions far below 1 per cent in relation to the HCl content of the undegraded PVC) can also be measured exactly. *Figure 1* shows the scheme of such an apparatus which is suitable for the determination in an inert atmosphere or in air. The vessel can be constructed in such a way that it can also be used for the degradation of dissolved samples[57].

In contrast to such equipment measurement of the pressure of the HCl split off is not so sensitive. At higher temperatures other volatile products besides HCl can also be formed so that additional difficulties can arise. Thermal analysis up to now has been used mainly for physical investigations of PVC whereas it is useful for application to the chemical degradation only in special cases[51].
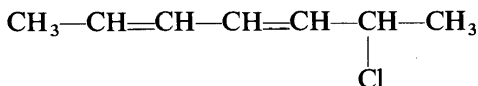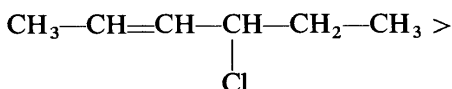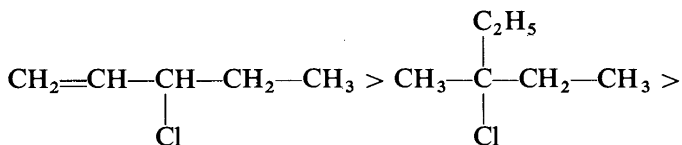
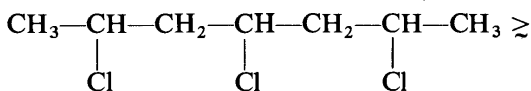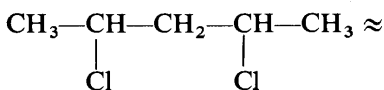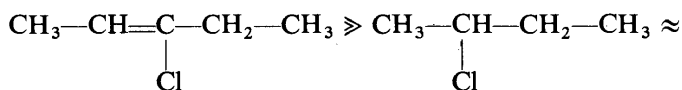## 3. INITIAL SITES OF DEHYDROCHLORINATION

A very important part of the dehydrochlorination of PVC is the initial step, which requires a relatively high activation energy. From model investigations with 2,4-dichloroalkanes, e.g. 2,4-dichloropentane, it follows that the normal undisturbed PVC-chain is not very sensitive to heat[13, 14]. Therefore in the literature various structural irregularities are discussed as initiation sites of the dehydrochlorination:

1. Chain end groups with initiator residues or unsaturated end groups
2. Branch points with tertiary chlorine atoms
3. Random unsaturation with allylic chlorine atoms
4. Oxidation structures
5. Head-to-head units.

3.1. Investigations with low molecular model compounds

For clarification of the nature of the initiation sites of the dehydrochlorination, experiments with low molecular models for PVC and for the various structural irregularities can be used. In the literature there is much data which of course was not always determined with respect to PVC degradation[15]. From recent investigations with 2-chlorobutane, 2,4-dichloropentane and 2,4,6-trichloroheptane[15] it can be concluded that the normal monomer units in PVC are thermally quite stable and that the dehydrochlorination of the models requires about 50 kcal/mole activation energy for the pyrolysis at about 350° to 400°. In contrast 4-chloro-2-pentene is thermally far less

stable than 3-chloro-1-pentene, which suggests that unsaturated chain end groups do not have an important influence on the thermal stability of PVC, whereas random isolated double bonds with allylic chlorine atoms are rather unstable. However it should be mentioned that there are remarkable differences in the values for the activation energy and the rate constants between the various investigators. For the stability of the most important model compounds between 200° and 400° the following order is valid:

$$CH_3—CH\!=\!\underset{\underset{Cl}{|}}{C}—CH_2—CH_3 \gg CH_3—\underset{\underset{Cl}{|}}{CH}—CH_2—CH_3 \approx$$

$$CH_3—\underset{\underset{Cl}{|}}{CH}—CH_2—\underset{\underset{Cl}{|}}{CH}—CH_3 \approx$$

$$CH_3—\underset{\underset{Cl}{|}}{CH}—CH_2—\underset{\underset{Cl}{|}}{CH}—CH_2—\underset{\underset{Cl}{|}}{CH}—CH_3 \gtrsim$$

$$CH_2\!=\!CH—\underset{\underset{Cl}{|}}{CH}—CH_2—CH_3 > CH_3—\overset{\overset{C_2H_5}{|}}{\underset{\underset{Cl}{|}}{C}}—CH_2—CH_3 >$$

$$CH_3—CH\!=\!CH—\underset{\underset{Cl}{|}}{CH}—CH_2—CH_3 >$$

$$CH_3—CH\!=\!CH—CH\!=\!CH—\underset{\underset{Cl}{|}}{CH}—CH_3$$

From these investigations it follows that random allylic chlorine atoms or branches with tertiary chlorine atoms are mainly responsible for the initiation of the thermal dehydrochlorination of PVC.

3.2. Branches in PVC

For a long time branches in PVC were discussed as the reason for the low thermal stability. Cotman was the first who reduced PVC with lithium aluminium hydride and obtained a polyethylene-like product; from ir-spectra using the ratio of methyl groups to methylene groups he determined the number of branches[16]. This method was later used by many authors but the results were not very exact because the peak of the methyl-group at 1378 cm^{-1} is seen just as a shoulder of the peak of the methylene group at 1370 cm^{-1}. This may be the reason why the figures for branching in the literature differ between about 0.5 and 20 methyl groups per 1000 C-atoms (see example in reference 17). More exact values can be obtained by ir-spectroscopic compensation of the reduced PVC against linear polymethylene[18, 19]. Depending on the preparation of the polymer about 5 to 15 CH_3—groups per 1000 C-atoms are found. The spectra of the reduced PVC also show random

trans-vinylene groups at 960 cm^{-1} in about the same amount as the CH$_3$– groups[19] (*Figure 2*).

Whereas the occurrence of branches in PVC is recognised nowadays the structure of the branch points is not quite clear. Caraculacu[20] did not obtain any indications of tertiary chlorine atoms in PVC during his investigations with copolymers of vinyl chloride and 2-chloropropene. Also investigations with copolymers of vinyl chloride and 2,4-dichloropentene-1 led to the conclusion[21] that due to steric reasons PVC should not contain branch points with tertiary chlorine atoms. Braun and Weiss[22,23] confirmed these findings by further investigations with copolymers from vinyl chloride and
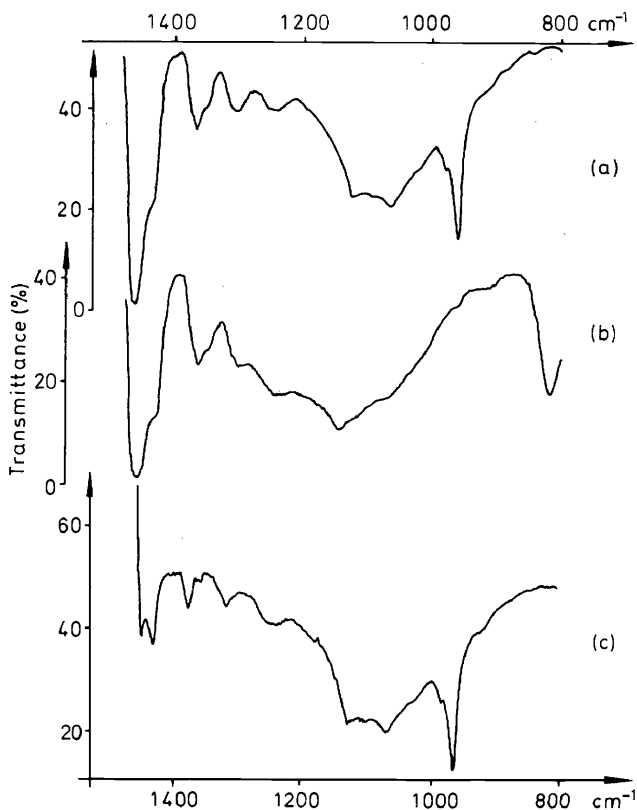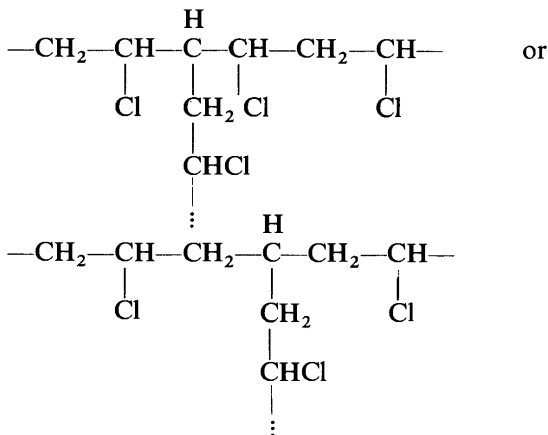

Figure 2. IR-spectra of reduced PVC (a) before, (b) after treatment with bromine vapour; (c) reduced PVC compensated against polymethylene.

2-chloropropene. The thermal degradation of such copolymers, with the same content of methyl groups as of branch points in radically prepared PVC, is much faster; also the distribution of the formed polyene sequences of different length is quite different from that of PVC, after the same degree of conversion. In the copolymers there is a remarkable shift to shorter polyene

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sequences. This, together with the finding that there is no relationship between the number of branch points and the rate of degradation[19], makes structures with tertiary chlorine atoms seem to be very unlikely. Other groups such as:

$$-CH_2-CH-\underset{\underset{\underset{\vdots}{CHCl}}{\underset{CH_2}{|}}}{\overset{H}{C}}-CH-CH_2-CH- \quad \text{or}$$

with Cl on first CH, CH$_2$ and Cl on branch, Cl on last CH

$$-CH_2-CH-CH_2-\underset{\underset{\underset{\vdots}{CHCl}}{\underset{CH_2}{|}}}{\overset{H}{C}}-CH_2-CH-$$

with Cl on first CH, Cl on last CH

should be much more stable to heat. Therefore one can conclude that PVC contains branches, but that these groups are not important for the initiation of the thermal degradation[23]. This is also in agreement with experiments of Gupta and St. Pierre[24] who found that copolymers of vinyl chloride and 2-chloropropene (**A**) are degraded much faster than those with 1-chloropropene (**B**). This means that tertiary chlorine atoms in the polymer chains are much more sensitive to heat than tertiary hydrogen atoms.

$$-CH_2-CHCl-\underset{\underset{CH_3}{|}}{\overset{H}{C}}-CHCl-CH_2-CHCl-$$
B

$$-CH_2-CHCl-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2-CHCl-$$
A
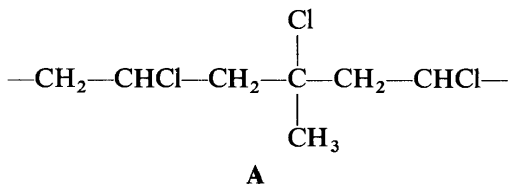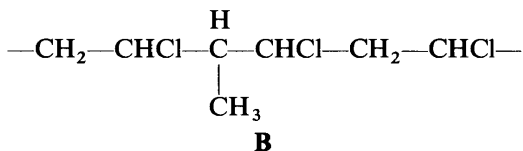
It should be mentioned here that up to now nothing is known about the presence and the structure of long chain branches in PVC which could be formed during the polymerization, at higher degrees of conversion, by chain transfer.

3.3. End groups

In the older literature many authors discussed the possibility of the initiation of the dehydrochlorination at the chain ends of PVC macromolecules. In some publications a reverse proportionality between molecular

weight and rate of degradation was found. However these results are not conclusive, as some authors did not find any relationship between molecular weight and rate of degradation of fractions of PVC (see Geddes, reference 1).

End groups can be formed from initiator residues or by chain transfer termination. Although this is reported for different rates of thermal degradation of PVC prepared with various initiators, the results of these investigations are not easily understood; very often the molecular weights of the samples investigated are not comparable; very often there is no information about other structural irregularities.

Some importance may be attached to the influence of unsaturated end groups. Bengough[25] determined such groups qualitatively by ir-spectroscopy using an ester-exchange method, by reacting allylic chlorine atoms with cadmium acetate and pyridine. However the role of unsaturated end groups as initiation sites for degradation is not supported by the experiments with low molecular model compounds (see Section 3.1.).

Finally one should expect that, with the dehydrochlorination starting at the end groups of the PVC molecules, the polyene sequences should also be formed at the chain ends. However the oxidative degradation of the original PVC results in a remarkable decrease in the average molecular weight, which cannot be due to the effect of the end groups. The oxidative cleavage of heat degraded PVC also results in a decrease in the molecular weight by about the same amount as with the original PVC[26]. All these findings do not support the theory of initiation of dehydrochlorination at the unsaturated end groups of the PVC macromolecules.

3.4. Random unsaturation in PVC

As the above mentioned investigations did not give clear results on the initiation of the dehydrochlorination of PVC at end groups or branches it was necessary to look for other initiation sites. In this respect primarily unsaturated groups with allylic chlorine have to be discussed. The above mentioned experiments (3.1.) with low molecular model compounds have shown that such structures are thermally much more labile than unsaturated end groups. Also from degradation investigations with vinyl chloride–vinyl bromide copolymers it was found, that below 200° the initiation of the dehydrochlorination cannot occur on normal vinyl chloride monomer-units but instead on positions with allyl chloride structure[27].

Very recently a direct experimental proof for the relationship between the thermal stability of PVC and the content of random unsaturated groups could be obtained[28]. During the oxidative degradation of PVC, using potassium permanganate in dimethylacetamide, it was found, viscosimetrically, that at 20°, after about 100 hrs, a constant final value for the molecular weight was reached. It is possible from these figures to calculate the number of cleavages per molecule. *Figure 3* shows, for fractions of a bulk PVC, that the number of cleavages is independent of the molecular weight. In the lower part of this figure can be seen that this also holds for the rate of thermal degradation at 180°. With technical suspension PVC samples of various sources a relationship between the number of cleavages, or the rate of degradation, and the molecular weight was found. (*Figure 4*). Here a clear connection between the number of cleavages and the rate of the
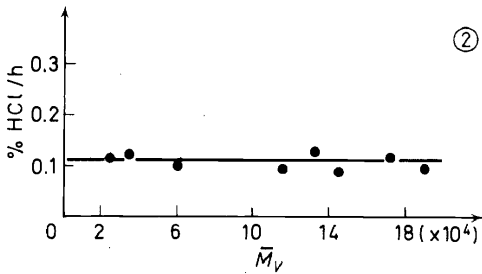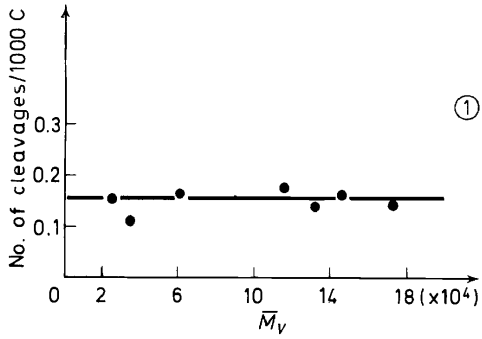
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Figure 3. Number of oxidative cleavable sites in fractions of bulk PVC and rate of thermal dehydrochlorination at 180°, under nitrogen.
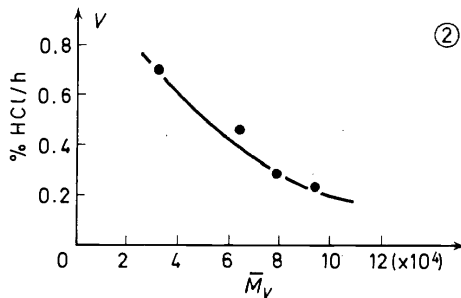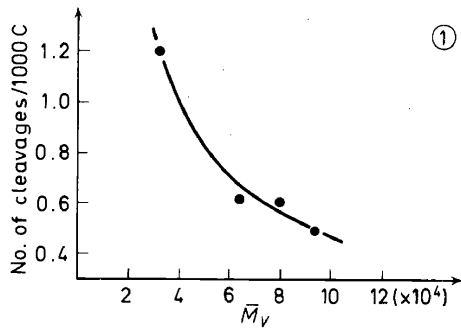

Figure 4. Number of cleavable sites (1) and rate of thermal degredation (2) for various technical suspension PVC types at 180° under nitrogen.

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dehydrochlorination can be seen (*Figure 5*) which shows the great importance of unsaturated groups within the polymer chains. After a careful chlorination of these double bonds an increase in the thermal stability was observed, and the number of double bonds found by oxidation was reduced.

Further it can be shown that, in the initial stage of the thermal dehydrochlorination, one polyene sequence is formed from each isolated double bond.
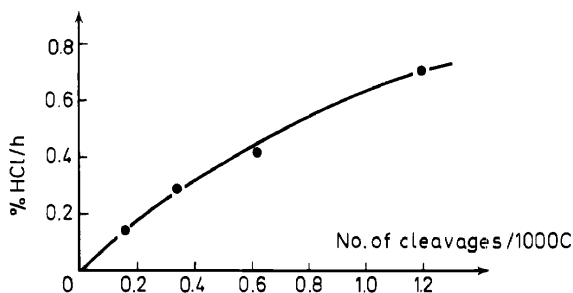

Figure 5. Rate of dehydrochlorination of suspension PVC at 180° under nitrogen in relation to the number of cleavable sites.

After one hour of degradation at 180° the same decrease in molecular weight is shown after oxidation in solution by potassium permanganate as after oxidation of the thermically untreated material. From the amount of HCl evolved and the number of cleavages the average length of the polyene sequences can be calculated, which is in good agreement with the spectroscopically obtained values[4].

3.5. Other Initiation Sites

As alternative initiation sites of the dehydrochlorination considered in the literature, oxidation structures are primarily discussed. By oxidation with oxygen or ozone, hydroperoxide or peroxide groups can be formed in PVC[29, 30]. As degradation products from these peroxide groups, carbonyl bands can be seen in the ir-spectra of the polymer[31]. However up to now only very little is known about the influence of such groups on the thermal stability of PVC. It is possible that the radicals formed during the decomposition of the peroxides can influence the degradation process and can possibly initiate a radical dehydrochlorination (see Geddes[1]). Another possibility for the initiation of the dehydrochlorination of PVC are head-to-head units, but up to now there is no experimental proof for the existence of such groups in PVC. Investigations with chlorinated trans-1,4-polybutadiene led to the conclusion that vicinal chlorine atoms in PVC should be less stable than those in 1,3-positions[32, 33]. The groups formed at the beginning of the degradation of head-to-head units,

$$—CH_2—CH—CH—CH_2— \qquad —CH_2—CH{=}C—CH_2—$$
$$\qquad \quad | \qquad | \qquad \xrightarrow{\qquad} \qquad \qquad \qquad |$$
$$\qquad \quad Cl \quad Cl \qquad \qquad \qquad \qquad \qquad Cl$$

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in analogy to the corresponding low molecular model compounds, are more stable than allylic chlorine atoms. Therefore the degradation begins at lower temperatures, as in the case of PVC, but also has a slower rate[33].

Finally it should be mentioned that up to now we do not have enough information about the influence of the stereoregularity of PVC on its thermal behaviour. It seems that with an increasing number of syndiotactic links the thermal stability is also increasing. However this can also be due to the higher crystallinity and the higher melting temperature of these samples.

4. DISCOLOURATION DURING THE DEHYDROCHLORINATION OF PVC

Nowadays it is quite clear that the discolouration during the thermal degradation of PVC is connected with the formation of sequences of conjugated double bonds within the polymer chains. With increased splitting off of HCl the colour becomes more and more intense, but exact quantitative relationships between colour and amount of evolved HCl are not yet known. By spectroscopy in visible and uv-range, conclusions can be drawn about the length and frequency distribution of the polyene sequences of different length[34].

Thermally degraded PVC shows, in the uv and visible part of the absorption spectra, about ten to twelve, not very well resolved, absorption maxima.
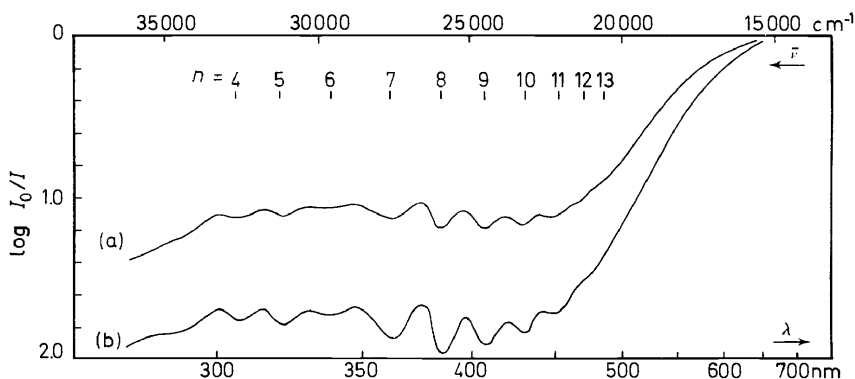

Figure 6. Absorption spectrum of PVC in tetrahydrofuran after thermal degradation at 170° under nitrogen. Degree of conversion: (a) 0.19 %, (b) 0.35 %. The absorption maxima correspond to polyene sequences with $n = 4, 5, 6$ etc. double bonds.

In *Figure 6* the spectrum of a thermally degraded PVC in tetrahydrofuran is given. Such spectra can be analysed assuming that the observed maxima are related to the main absorption band of the different polyene sequences.

The absorption spectrum of a polyene with double bonds consists of several sharp bands, of which, for $n \geqslant 5$, the band of the longest wavelength has the highest intensity. With increasing number of double bonds the total system of bonds is shifted to longer wavelengths. At the same time its intensity also increases which follows, for example, from the spectra of unsubstituted polyenes[35].

It is known, that between the number of double bonds and the wavelength

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λ of the absorption maximum, at the longest wavelength of a polyene, the so-called square root law is valid.

$$\lambda = k.\sqrt{n} + k'$$

In this equation the end groups of the polyene can be considered by adding so-called double bonding equivalents, for example for the phenyl group 1.5 and for the carboxy group 0.8. For identifying the absorption maxima in the spectrum of degraded PVC the function $\lambda = f(\sqrt{n})$ for dimethylpolyenes can be used; in this relationship the absorption maxima of degraded PVC fit very well, at least in the range of longer sequences[34].

Because no spectra of model compounds for polyene sequences in PVC are known one can try to apply the regularities found on various classes of polyenes. The following prerequisites can be used which are generally valid for polyenes:

(a) the relation between the absorption maxima and the number of double bonds is given by the square root law;
(b) the extinction coefficient ε_n of the main band of a polyene is directly proportional to the number of double bonds n:

$$\varepsilon_n = \varepsilon_g \times n$$

whereas ε_g (1 mole^{-1} cm^{-1}) is a constant and ε_n (1 mole^{-1} cm^{-1}) is the decadic extinction coefficient. It has to be taken into account that the absorption at a maximum in the PVC spectrum is not only due to the main maximum of the corresponding polyene sequence. In addition the absorptions of the following longer polyene sequences absorb at the same wavelength. This amount is in the same order of magnitude as the absorption of the main maximum of the corresponding polyene sequence. But Krauss and Grund[36] found in the spectra of ω-phenyl polyenales in chloroform that in this case the proportionality between ε_n and n is also given for the maximum of the complete undissolved system of bands. If one presumes that the extinction of the absorption maxima in the spectra of degraded PVC are all caused by the band with the longest wavelength, all concentrations of polyenes are calculated somewhat too high by about the same factor. But the relative concentrations of the polyene sequences of various lengths are quite exact.

The frequency of the polyene sequences of different lengths can be calculated using the Lambert–Beer law. Thereby x is the conversion during the degradation (ratio of the split off HCl to the HCl content of the undegraded polymer), c_p (g/1) is the concentration of the polymer in solution, I_0 and I are the light intensities and c is the cell path. Then the following equation can be deduced:

$$H'_n = \frac{\log I_0/I}{dnxc_p}$$

H'_n is a relative measure for the frequency of the polyene sequences with n double bonds in the special degraded PVC. All values in this equation are either known or can be directly measured. It should be noted that due to the constants which are incorporated in H'_n only the values for a single polymer can be directly compared, but not those of different polymer samples.

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Using this method the frequency of the polyene sequences was calculated from the electron spectra of degraded PVC. This is shown in *Figure 7* for a sample which was degraded at 170° in nitrogen to a conversion of $x = 0.165 \times 10^{-2}$. It can be seen that the frequency of the polyene sequences rapidly becomes smaller with increasing number of conjugated double bonds. It can be extrapolated that the longest sequences have about 25 to 30 double bonds.
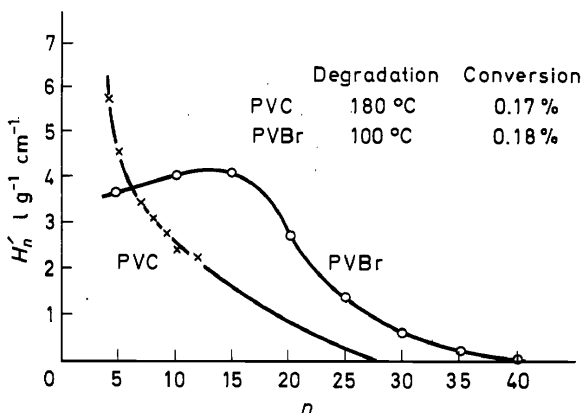

Figure 7. Frequency distribution H'_n of polyene sequences in partially degraded polyvinyl chloride and polyvinyl bromide according to reference 34.

In the same way also the degraded polyvinyl bromide can be investigated. Here the average sequence length is much higher than in the case of PVC. Sequences with about 12 to 14 double bonds are most frequently found; the longest have about 40 to 45 double bonds.

Several other authors also reported about similar short average polyene sequences at the beginning of the PVC degradation[38, 39]. Geddes[38] calculated from the amount of HCl split off and from the determination of the number of polyene sequences, by ozonolyses, average sequence lengths of about 10 to 15.

From the analyses of the spectra it follows that polyene sequences of various length are formed during the degradation. For an understanding of the mechanism of the dehydrochlorination it is important to know whether the sequence length distribution is changed with increasing conversion. From the spectra of such PVC samples it follows that, besides a small shift of the frequency distribution to shorter sequences, with increasing conversion the spectroscopically found polyene concentration decreases.

It can be concluded, from the change in the frequency distribution of the polyene sequences with increasing conversion, that the polyene sequences undergo further reactions during the thermal degradation. Besides cross-linking, aromatic hydrocarbons, such as benzene and toluene, are formed and the ir-spectra of the polymers show aromatic structures[37]. The shift of the frequency distribution in favour of shorter sequence lengths makes it probable

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that preferably the longer sequences undergo such secondary reactions. Due to this shift of the frequency distribution no simple relationship between colour and degree of degradation of PVC can be expected.

With increasing temperature a shift of the frequency distribution to shorter sequences is also observed[40]. Under no circumstances are polyene sequences of remarkably greater lengths formed. This means that for the mechanism of the dehydrochlorination of PVC the degradation must start on many sites simultaneously. With increasing time of degradation or with increasing conversion the number of polyene sequences becomes greater, but not their length. The zipper-like dehydrochlorination of PVC is stopped after the formation of sequences with up to 20–25 double bonds.

Also, calculations of the dehydrochlorination kinetics of PVC and the length distribution of the polyene sequences by Kelen et al.[41, 42] are in good agreement with the experimental results.

If during the degradation the split off HCl is not completely removed, deeply coloured complexes of HCl and the polyene are formed[43]:

$$\begin{array}{c} /CH_2 \diagdown CH / \begin{array}{c} CH \\ \diagup \end{array} \diagdown CH / \begin{array}{c} CH \\ \diagup \end{array} \diagdown CH / \begin{array}{c} CH \\ \diagup \end{array} \diagdown CH_2 \\ | \\ Cl \end{array}$$

$$\xrightarrow{HCl} \left[\begin{array}{c} CH_2 \\ \diagup \diagdown \\ CH \end{array} \diagdown \begin{array}{c} \overset{+}{CH} \\ \diagup \diagdown \\ CH \end{array} \diagdown \begin{array}{c} CH \\ /\!/ \diagdown \\ CH \end{array} \diagdown \begin{array}{c} CH \\ /\!/ \diagdown \\ CH_3 \end{array} \right]^+ Cl^-$$
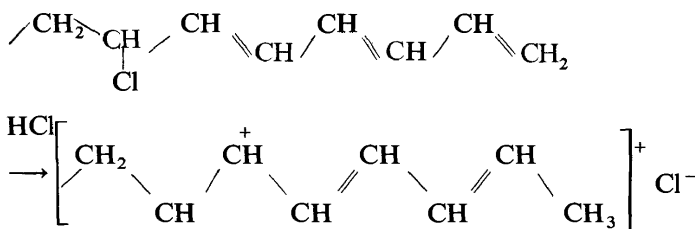
By the superposition of the blue coloured complexes with yellow to brown coloured free polyene sequences, blue to olive discolourations of the polymers are obtained. The complex formation is a reversible reaction; after swelling in benzene the complexes can be destroyed with ammonia and can be regenerated with HCl. Also basic stabilizers, such as cadmium stearate, react with the complexes bleaching the samples. These results are also of practical importance because, under technical conditions, the split off HCl will not be removed completely from the samples. This is only possible with small samples, in solution or in very thin films. Thus Thallmaier and Braun[40] observed on thin films of suspension-PVC after the degradation at 170°, the same spectra as on samples dissolved in tetrahydrofuran.

Also, Onozuka and Asahina[3] discussed charge-transfer complexes as the reason for the discolouration of PVC and have shown the analogue's complex formation with model compounds.
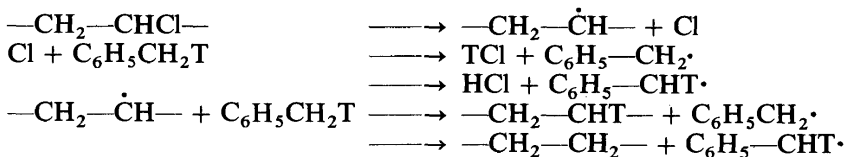
5. MECHANISM OF THE THERMAL DEHYDROCHLORINATION OF PVC

For the thermal dehydrochlorination of PVC, radical, ionic and unimolecular elimination mechanisms have been discussed. A clear decision is not yet possible and there are many contradictory results in the literature. Also the experimental conditions and the history of the polymer sample play an important role and it is possible that in special temperature ranges various mechanisms are effective, side by side.

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5.1. Radical mechanism

In the older literature many formulations for the radical mechanism of the thermal degradation of PVC are given. Experiments of Bengough and other authors[48] have shown that inhibitors of radical reactions do not influence the PVC degradation, which is not in favour of a radical mechanism.

Thermally strongly degraded PVC gives an esr-spectrum with one narrow line having a g-value similar to that of the free electron[29]. The reason for this paramagnetism must probably be seen in the conjugated structure of the network formed at higher degrees of conversion. However, from the esr-spectra no hints for a radical nature of the elimination process can be found. Bamford and Fenton[50] investigated the degradation of PVC in tritium labelled toluene with CH_2T-groups. They explained the observed incorporation of tritium into the polymer by the following mechanism:

$$-CH_2-CHCl- \longrightarrow -CH_2-\overset{\cdot}{C}H- + Cl$$
$$Cl + C_6H_5CH_2T \longrightarrow TCl + C_6H_5-CH_2\cdot$$
$$\longrightarrow HCl + C_6H_5-CHT\cdot$$
$$-CH_2-\overset{\cdot}{C}H- + C_6H_5CH_2T \longrightarrow -CH_2-CHT- + C_6H_5CH_2\cdot$$
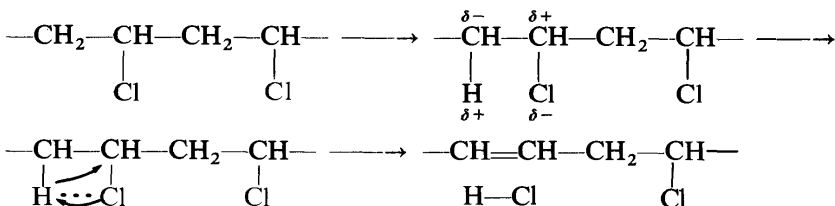$$\longrightarrow -CH_2-CH_2- + C_6H_5-CHT\cdot$$

From these and some other investigations the authors concluded that the mechanism of the PVC degradation is a radical one.

By thermal volatilization analysis of mixtures of PVC and some other polymers, e.g. polymethyl methacrylate, a retardation of the initial HCl splitting off is always observed. This was explained by a reaction between the radicals from PVC and radical fragments from other polymer due to a radical nature of the PVC degradation[51].

5.2. Ionic mechanism

The dehydrochlorination of PVC by bases such as lithium chloride and dimethyl formamide follows an ionic mechanism[52]. Also sulphuric acid[53] or some heavy metal salts, especially iron salts, accelerate the dehydrochlorination. Baum[54] and later on Rieche et al.[55] also discussed an ionic mechanism for the pure thermal dehydrochlorination and thus explained the strong catalytic effect of organic bases. However up to now there is no direct proof for such a mechanism and the experimental findings as well as theoretical considerations are contrary to this theory. Imoto and Nakaya[56] proposed an elimination mechanism with a cyclic transition state from calculations of the bonding energy of C–Cl bondings:

$$-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}- \longrightarrow -\overset{\delta-}{CH}-\overset{\delta+}{\underset{\underset{\delta-}{Cl}}{\underset{|}{CH}}}-CH_2-\underset{\underset{Cl}{|}}{CH}- \longrightarrow$$

$$-\underset{\underset{H\cdots Cl}{|}}{CH}-\underset{|}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}- \longrightarrow -CH=CH-CH_2-\underset{\underset{Cl}{|}}{CH}-$$
$$\qquad\qquad\qquad\qquad\qquad\qquad H-Cl$$

This mechanism is supported by many experiments[57]: The thermal degradation of PVC in inert solvents is not influenced by inhibitors for radical reactions[48]; hydroquinone gives no inhibition in the absence of oxygen;
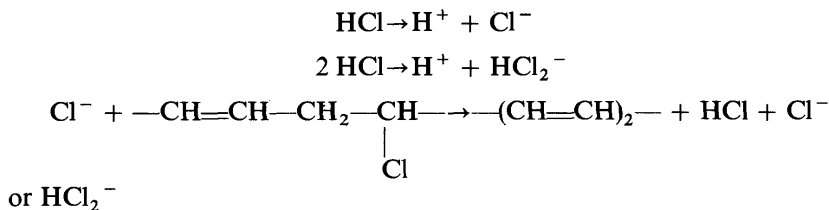
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the autocatalysis of the thermal dehydrochlorination of PVC by HCl (see Section 5.3.) is scarcely in agreement with the radical mechanism. There is a relationship between the rate of degradation in solution and the dielectric constant of the solvent[2] which is characteristic for a non-radical reaction. Also, the kinetics of the degradation in inert solvents with a first order rate law[57, 58] and the behaviour of PVC during the degradation in phenolic solvents[59] are in line with the cyclic elimination mechanism.

Of course in the presence of basic compounds, e.g. in dimethyl formamide solution[60], other mechanisms are possible. At higher temperatures or in the presence of oxygen or peroxides[45] radical reactions are probable, but up to now this has not yet been completely investigated.

5.3. Influence of hydrogen chloride

The influence of hydrogen chloride on the thermal dehydrochlorination of PVC was, for a long time, a matter of dispute. But in nearly all more recent publications a catalytic acceleration of the degradation by HCl was observed (compare with the older literature, see Geddes[1]). Talamini et al. showed this for the degradation of solid PVC[61]; Braun and Bender[57] observed a higher rate of dehydrochlorination in ethyl benzoate in the presence of free HCl and also a more intensive discolouration without formation of polyene-HCl complexes·

The mechanism of the effect of HCl on the PVC degradation is not yet clear. Below 200° a dissociation of HCl into free radicals is not very probable. Van der Ven and de Witt[62] therefore discuss the dissociation of HCl under formation of Cl^-- or $HCl_2{}^-$-ions, which as bases accelerate the dehydrochlorination:

$$HCl \rightarrow H^+ + Cl^-$$

$$2\,HCl \rightarrow H^+ + HCl_2{}^-$$

$$Cl^- + -CH{=}CH-CH_2-\underset{\underset{Cl}{|}}{CH}- \rightarrow -(CH{=}CH)_2- + HCl + Cl^-$$

or $HCl_2{}^-$

Morikawa[63] supposes that HCl reacts with double bonds in degraded PVC and influences the degradation in this way:
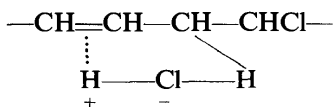

Thus the mechanism of the catalysis of PVC degradation by HCl is not completely clear, but the accelerating effect of HCl is beyond doubt. Under the conditions of technical PVC processing HCl is therefore important not only for the degradation but also for the discolouration.

5.4. Termination of the growth of the polyene sequences

The formation of polyene sequences during the dehydrochlorination can be understood on the basis of the rather high reactivity of the monomer units

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adjacent to the allylic chlorine atoms which are much more reactive than a normal monomer unit of the PVC chain:

$$-CH\!=\!CH\!-\!\underset{\underset{Cl}{|}}{CH}\!-\!CH_2-$$
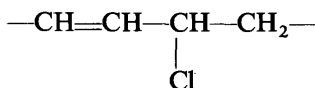
It is much more difficult to answer the question of why the polyene sequences normally only grow to a length of 5 to 10 conjugated double bonds. Supposing a radical mechanism for the degradation, this could be explained by a termination of the kinetic chain (see reference 1). Such a formulation is not possible for a non-radical process. It is also not very probable that the growth of the polyene sequences finishes at structural irregularities in the chains, because such groups seem to be present only in a very small amount. It can be thought that the allyl activation of the dehydrochlorination becomes smaller, the longer and the more stabilized by resonance the adjacent polyene sequence is. At a distinct length the energy for the dehydrochlorination and the energy content of the system by conjugation are about the same and the polyene formation does not continue. This could also explain the observation that polyvinyl bromide under the same condition gives much longer polyene sequences than PVC[34]. Due to the weaker C—Br bond compared with the C—Cl bond the resonance stabilization of the polyene requires longer sequences for the energetic balance.

At higher degrees of conversion the crosslinking of the chains may also be of importance, but at lower conversions (about 0.1 per cent) no crosslinking is obtained and on average there is only one polyene sequence per macromolecule. Thus up to now we have no final explanation for the formation of relatively short polyene sequences.

6. DEGRADATION IN PRESENCE OF OXYGEN

During the thermal degradation of PVC in the presence of oxygen three effects are known[1]:
1. Acceleration of the dehydrochlorination.
2. Bleaching of the degraded polymer.
3. Lowering of the molecular weight.

Most authors explain these findings by a superposition of radical and pure thermal reactions. By autoxidation, peroxidic macroradicals can be formed which, by transfer reactions, result in a branching of the kinetic chain. Valko has given the kinetic scheme for the degradation of PVC in the presence of oxygen and checked this by experiments[44]. The rate of degradation is not only dependent on the reaction of oxygen with the formed double bonds but also on the number of cleaved C—C bonds. The importance of peroxidic structures for the degradation of PVC was shown by Geddes: the hydroperoxidic groups obtained by ozonization result in a similar acceleration of PVC degradation, as does the presence of cumene hydroperoxide or other peroxides[45]. Very probably under this condition the reaction follows a radical mechanism[45].

The bleaching effect of oxygen on degraded PVC is due to a shift of the sequence length distribution to shorter sequences[46]. This can be seen from

the spectra of polymers which have been degraded in the presence of oxygen. These spectra do not show single absorption maxima which can be correlated to various polyene sequences[57]. Thus up to now it is not possible to discuss the polyene sequence length in PVC degraded in the presence of oxygen (*Figure 8*).
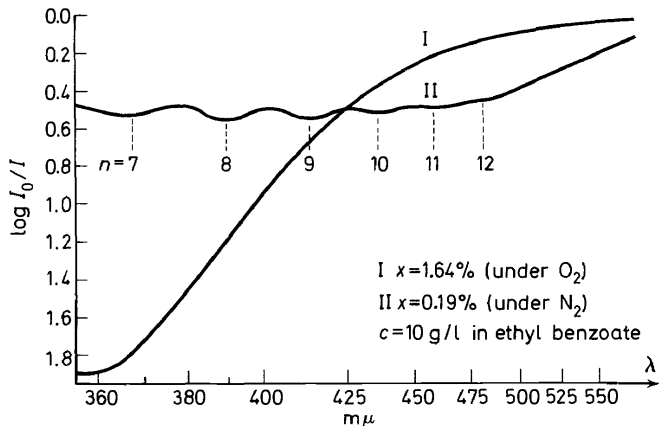

Figure 8. Spectrum of PVC after degradation for 90 min at 170°, in ethyl benzoate under oxygen and under nitrogen.

During the thermal oxidation of PVC at 105° the molecular weight is increased due to the beginning of crosslinking; here the presence of anti-oxidants has a retarding influence.

7. INFLUENCE OF PLASTICIZERS ON THE PVC DEGRADATION

The thermal stability of plasticized PVC is connected with the type and amount of the plasticizer. Wolkober[64] observed, by simultaneous measure-ment of the absorbed oxygen and the HCl evolution during the heating of plasticized PVC, that there is a strong dependence on the oxidation stability of the plasticizer. In many cases the oxygen uptake is faster than the dehydro-chlorination[65] and it must be concluded that the dehydrochlorination is influenced by peroxide products from the plasticizer[66,67,68]. Therefore many investigations were made recently on the thermal behaviour of plasti-cizers in the presence of oxygen, in part by use of the differential thermal analy-sis[69]. The rate of the dehydrochlorination depends on the amount of plasti-cizer in the PVC[70], but there was found to be no linear relationship between plasticizer content and rate of dehydrochlorination. For each plasticizer at a special concentration a minimum for the rate of degradation is found (*Figure 9*). It is possible that at lower concentrations the interactions between the polar groups in PVC and the plasticizer molecules are stronger than be-tween the PVC chains. Therefore in this range a higher degree of order is obtained than in the absence of plasticizers and thus a higher energy for the HCl splitting off would be necessary. Thus the solvation of the PVC chain by
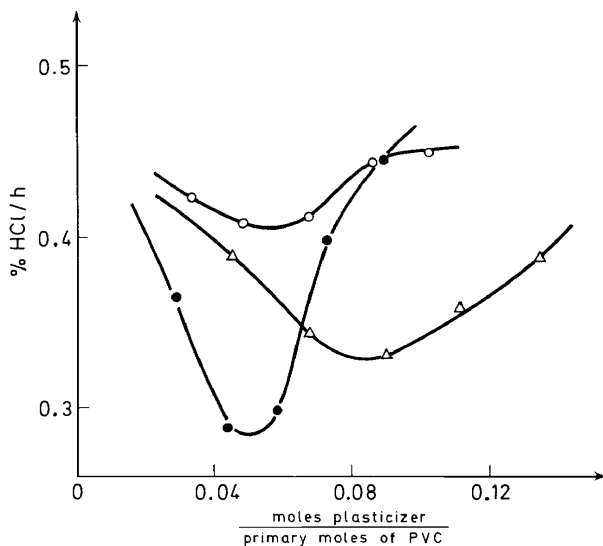
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Figure 9. Rate of dehydrochlorination of foils of plasticized PVC 180° under nitrogen. ● DOS Dioctyl sebacate, ○ TCP Tricresyl phosphate, △ DBP Dibutyl phthalate.

the plasticizer molecule could have some stabilizing effect. However a complete understanding of these interesting effects is still open.

8. CONCLUSIONS

In recent years remarkable progress was made in the field of basic research about the thermal degradation of PVC. From many experiments it is fairly clear nowadays that the degradation is initiated by allylic structures within the PVC chains. However it is not clear, up to now, how these structural irregularities are formed and what can be done to avoid their formation. It seems that the branches in PVC do not have such a great importance for the rate of degradation.

The mechanism of the thermal degradation is also not yet completely clear. Under inert conditions a unimolecular cyclic mechanism is very probable, but only a little is known about the degradation under practical conditions, e.g. in the presence of oxygen. The discolouration of PVC, nowadays, can be understood and described in a semiquantitative way by the length and and the frequency distribution of the polyene sequences.

Up to now we do not have quantitative relationships between colour and degree of degradation. Finally, the large field of the stabilization of PVC should be mentioned. Here we have very little knowledge about the reactions between PVC and stabilizers, and we need much more information which could also be useful for the development of new stabilizers for PVC.

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