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# Investigation of PVC Degradation Mechanism by ESR Spectroscopy

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## ABSTRACT

During the $\gamma$-irradiation and UV-light photolysis of poly(vinyl chloride) (PVC), free radicals are formed which may be detected by electron spin resonance (ESR) spectroscopy. In this paper interpretations of the ESR spectra and decomposition mechanisms of PVC are presented.

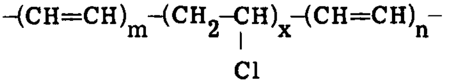
## INTRODUCTION

Influenced by heat, light, and ionizing radiation the mechanophysical properties of poly(vinyl chloride) (PVC) changes and its color turns yellow to reddish-brown. Discoloration and changes in mechanical properties are the results of a gradual degradation and crosslinking process. Dehydrochlorination followed by formation of polyene structures is the main reaction observed. In the presence of oxygen (air), additional oxidation reactions may occur. If these reactions occur by a free-radical mechanism, the intermediate free radicals are detectable by electron spin resonance (ESR) spectroscopy. This method can also identify free radicals if they exist in high enough concentrations under the experimental conditions. Interpretation of ESR spectra can be quite complicated when signals from different free radicals overlap. In spite of these difficulties, many ESR studies of degraded PVC have been published, but no complete and satisfactory interpretation of the decomposition mechanism of PVC has been offered. For the investigation of certain types of free radicals double resonance (ENDOR) is a very valuable method. The ENDOR method means the detection of changes in a monitored ESR signal due to the induction of nuclear resonance in nuclei coupled to the paramagnetic center. In this paper current results in the application of ESR spectroscopy to the study of PVC decomposition mechanisms are discussed.

## MECHANISM OF THE DECOMPOSITION OF PVC

Under physical and chemical treatment of PVC the main reaction observed is dehydrochlorination and formation of polyene structures. Different authors estimate the average length of the conjugated double bonds formed to be: 5-10 units [1], 4-12 units [2], 6-12 units [3], 4-16 units [4] depending on the experimental conditions and type of energy used.

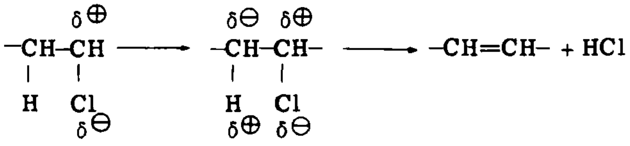
It has been shown that at the beginning of PVC decomposition, random dehydrochlorination of the polymer takes place [5]. In further steps, polyene sequences (m or n) grow until they reach reported maximum lengths of 10-16 units. A major problem is that it is impossible to determine experimentally the sequence distribution along the polymer chain (value of x):



$$-(CH{=}CH)_m-(CH_2-\underset{\underset{\displaystyle Cl}{|}}{C}H)_x-(CH{=}CH)_n-$$

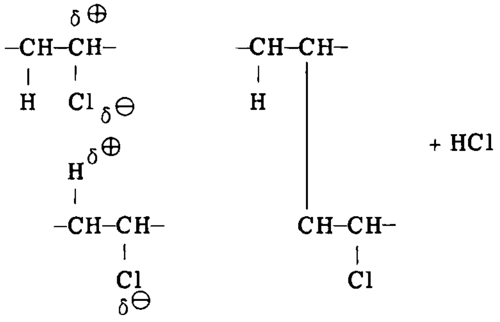
Two different mechanisms have been proposed for the formation of polyene structures: an ionic mechanism [5-15] and a radical mechanism [5, 7, 11, 16-24].

The intramolecular ionic mechanism occurs with evolution of HCl but without formation of free radicals:



$$-\underset{\underset{\displaystyle H}{|}}{CH}-\overset{\delta\oplus}{\underset{\underset{\displaystyle \underset{\delta\ominus}{Cl}}{|}}{CH}} \longrightarrow -\overset{\delta\ominus}{\underset{\underset{\displaystyle \underset{\delta\oplus}{H}}{|}}{CH}}-\overset{\delta\oplus}{\underset{\underset{\displaystyle \underset{\delta\ominus}{Cl}}{|}}{CH}}- \longrightarrow -CH{=}CH- + HCl \qquad (1)$$

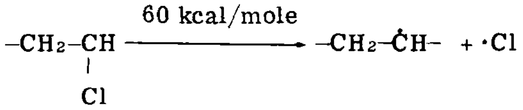
An intermolecular dehydrochlorination reaction leading to crosslinking can also be considered:



(2)

However, the intramolecular reaction with formation of polyene sequences is the preferred reaction. The activation energy for the dehydrochlorination probably goes through a minimum as the length of the polyene sequences increases.

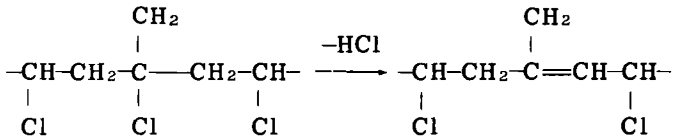
The free-radical decomposition of PVC occurs by the following mechanism:



$$-CH_2-\underset{\underset{\displaystyle Cl}{|}}{CH} \xrightarrow{60\ \mathrm{kcal/mole}} -CH_2-\dot{C}H- + \cdot Cl \qquad (3)$$

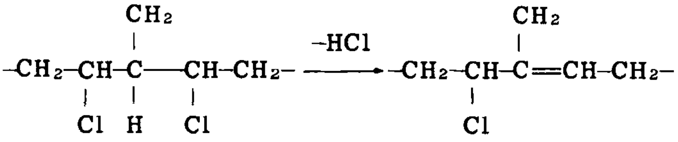
The bond dissociation energy for the cleavage of an CH–Cl bond is approximately 60 kcal/mole. Investigation of thermal decomposition of model compounds and a detailed study of the various molecular structures present in commercial PVC has shown that the chloroallylic groups are the most reactive [14].

The effects of branching on the thermal stability of PVC [25-29] indicate that the tertiary bonded chlorine and the allylic chlorine are more susceptible to thermal degradation than secondary chlorine. It thus seems reasonable that the structures I and/or II if present, would be the main contributors in the initiation of thermal decomposition of PVC at processing temperatures:



$$-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_2-\overset{\displaystyle CH_2}{\overset{|}{\underset{\underset{\displaystyle Cl}{|}}{C}}}-CH_2-\underset{\underset{\displaystyle Cl}{|}}{CH}- \xrightarrow{-HCl} -\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_2-\overset{\displaystyle CH_2}{\overset{|}{C}}=CH-\underset{\underset{\displaystyle Cl}{|}}{CH}- \qquad (4)$$

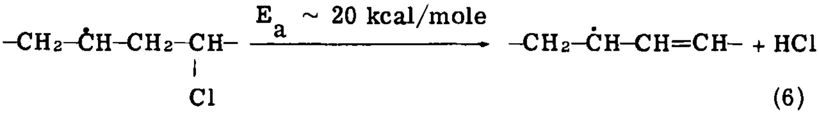
I



$$-CH_2-\underset{Cl}{CH}-\overset{CH_2}{\underset{H}{C}}-\underset{Cl}{CH}-CH_2- \xrightarrow{-HCl} -CH_2-\underset{Cl}{CH}-\overset{CH_2}{C}=CH-CH_2- \qquad (5)$$

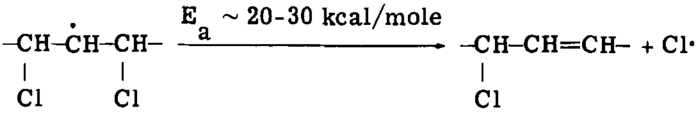
II

The activation energies determined for the dehydrochlorination reaction vary from 20 to 36 kcal/mole depending on experimental conditions and polymer structure [30]. The evolution of HCl from macroradicals has a lower activation energy than bond cleavage with formation of Cl• and H• free radicals:



$$-CH_2-\dot{C}H-CH_2-\underset{Cl}{CH}- \xrightarrow{E_a \sim 20\text{ kcal/mole}} -CH_2-\dot{C}H-CH=CH- + HCl \qquad (6)$$

$$-CH_2-\dot{C}H-CH_2- \xrightarrow{E_a \sim 40\text{ kcal/mole}} -CH_2-CH=CH- + H\cdot \qquad (7)$$



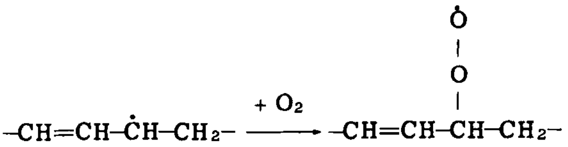
$$-\underset{Cl}{CH}-\dot{C}H-\underset{Cl}{CH}- \xrightarrow{E_a \sim 20\text{-}30\text{ kcal/mole}} -\underset{Cl}{CH}-CH=CH- + Cl\cdot \qquad (8)$$

The elimination of the first HCl molecule with formation of an allylic radical is more rapid than each subsequent elimination step leading to polyenyl structures.

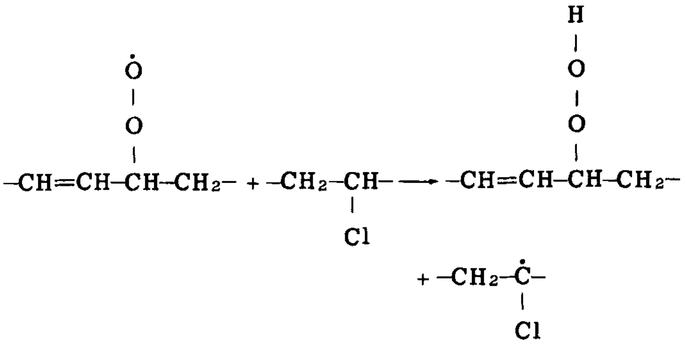
The dehydrochlorination process of PVC is generally recognized to be catalyzed by HCl present in the atmosphere, in solutions in contact with the material or accumulated in the solid polymer sample because of hindered diffusion [11, 13-15, 31-33]. Large differences in particle size have been found to influence the course of the PVC degradation [19, 34].

It has been found that the presence of oxygen causes a faster dehydrochlorination [12, 19, 28, 34-36] and a less intense discoloration [12, 37] due to shorter polyene sequences and chain scission reactions [6, 34].

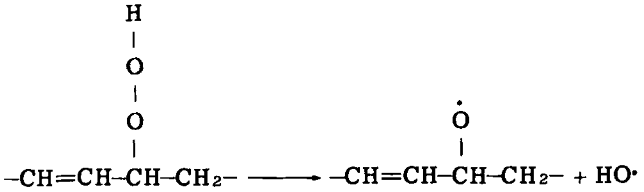
Chain scission reactions occur by a mechanism in which oxygen attacks a growing polyene sequence.



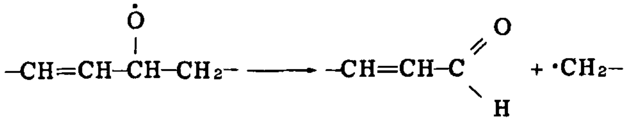
$$-CH{=}CH{-}\dot{C}H{-}CH_2- \xrightarrow{+\,O_2} -CH{=}CH{-}\overset{\begin{array}{c}\dot{O}\\|\\O\\|\end{array}}{C}H{-}CH_2- \qquad (9)$$



$$-CH{=}CH{-}\overset{\begin{array}{c}\dot{O}\\|\\O\\|\end{array}}{C}H{-}CH_2- + -CH_2{-}\underset{\begin{array}{c}|\\Cl\end{array}}{C}H- \longrightarrow -CH{=}CH{-}\overset{\begin{array}{c}H\\|\\O\\|\\O\\|\end{array}}{C}H{-}CH_2- + -CH_2{-}\underset{\begin{array}{c}|\\Cl\end{array}}{\dot{C}}- \qquad (10)$$

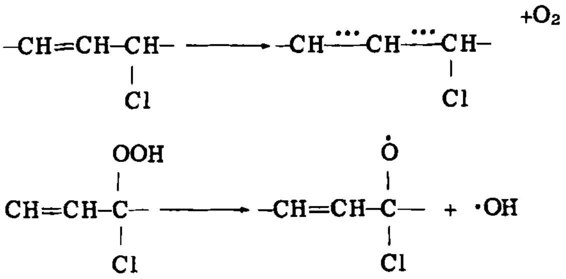


$$-CH{=}CH{-}\overset{\begin{array}{c}H\\|\\O\\|\\O\\|\end{array}}{C}H{-}CH_2- \longrightarrow -CH{=}CH{-}\overset{\begin{array}{c}\dot{O}\\|\end{array}}{C}H{-}CH_2- + HO\cdot \qquad (11)$$



$$-CH{=}CH{-}\overset{\begin{array}{c}\dot{O}\\|\end{array}}{C}H{-}CH_2- \longrightarrow -CH{=}CH{-}C\begin{array}{l}{/\!\!/}O\\ \diagdown H\end{array} + \cdot CH_2- \qquad (12)$$

One of the proposed mechanisms implies the formation of an intermediate allylic carbanion [38]:



$$-CH{=}CH{-}\underset{\begin{array}{c}|\\Cl\end{array}}{C}H- \longrightarrow -CH\overset{\cdots}{-}CH\overset{\cdots}{-}\underset{\begin{array}{c}|\\Cl\end{array}}{C}H- \quad +O_2$$

$$CH{=}CH{-}\overset{\begin{array}{c}OOH\\|\end{array}}{\underset{\begin{array}{c}|\\Cl\end{array}}{C}}- \longrightarrow -CH{=}CH{-}\overset{\begin{array}{c}\dot{O}\\|\end{array}}{\underset{\begin{array}{c}|\\Cl\end{array}}{C}}- + \cdot OH \qquad (13)$$

This reaction seems less probable from a thermodynamical point of view, because abstraction of hydrogen by molecular oxygen and formation of a hydroperoxide is an endothermical reaction which requires about 30 kcal/mole. When an attack by oxygen does occur it is preferentially at an allylic position, which can explain why oxygen decreases the length of the polyene sequences.

## ESR STUDIES OF THERMAL DECOMPOSITION OF PVC

PVC is known to have a two-step thermal decomposition. In the first stage, up to 400°C, dehydrochlorination reaction occurs, but above 400°C the carbonization (pyrolysis) with dehydrogenation is observed. The following ESR results have been obtained.

The shape of the signal is a singlet with gaussian line shape and the half width at half height 6 G and the g value 2.003 ± 0.0005.

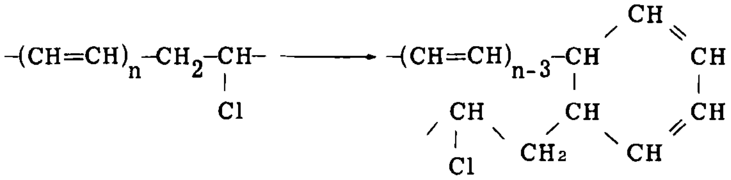
In the presence of air, the intensity of the ESR signals increase.

The ESR signal of a PVC sample heat-treated below 400°C either in air or in vacuum is easily saturated, when measured in vacuum at room temperature. When air is admitted to the sample, the degree of saturation decreases. This reaction is reversible. The apparent line intensity thus depends on the oxygen pressure.

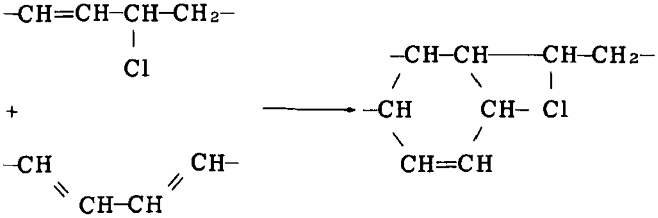
The ESR signal of the PVC, heat-treated above 400°C, is not as easily saturated and the effect of oxygen is the opposite, namely, the signal is decreased by admission of air and increased by evacuation.

It has been suggested [40, 41], after careful analysis of ESR spectra, that the single-line spectrum consists of components from three different free radicals. These were not identified. It is very difficult to assign these resolved ESR spectra components to alkyl or allyl polymer radicals, because they are very reactive at elevated temperatures and have a short life time. The half-life of alkyl radicals in PVC at room temperature in vacuo is about 4 sec [42]. The single line ESR spectrum is related mainly to free radicals formed during the dehydrochlorination reaction [1], where the unpaired electron is well delocalized along the conjugated double bonds [43].

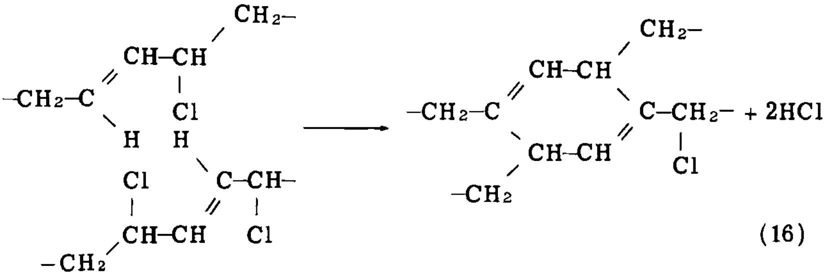
The decrease in saturation when oxygen is present is caused by a decrease in the spin-lattice relaxation time $T_1$. Above 200°C, the delocalization of the unpaired electron can be due to pseudo-aromatic structures formed by different mechanisms [13, 15, 31, 44]:



(14)



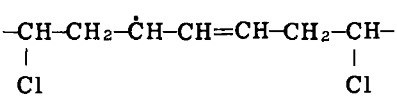
(15)



(16)

## ESR STUDIES OF DECOMPOSITION OF PVC BY IONIZING RADIATION

In the radiolysis of PVC, the predominant process in the formation of primary alkyl radicals is the homolysis of C–Cl bond. Electron and γ-irradiation of PVC sample at -196°C give a septet line-spectrum poorly resolved with a linewidth of 17 G and a hyperfine splitting constant of 18 G [45] (Fig. 1). This ESR spectrum has been attributed to the allylic radical (III):



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

III

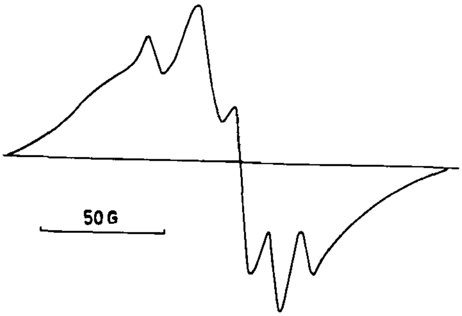


FIG. 1. ESR spectrum of $\gamma$-irradiated poly(vinyl chloride) at -196°C [45].

Room temperature annealing results in the loss of hyperfine structure, and formation of single line spectrum. During the annealing there may be a continuous evolution of HCl starting with the allylic radical (III) and producing polyene radicals (IV):

$-\dot{C}H-(CH{=}CH)_n-$

IV

It has been reported [41, 46] that during electron irradiation of PVC samples a poorly resolved six-line spectrum is obtained and attributed to polyalkyl radicals.

Ionizing irradiation of PVC samples at room temperatures gives a singlet line spectrum with a linewidth of 25 G which was attributed to polyene radicals (IV) [22, 47-49] (Fig. 2). Heavily irradiated PVC ( > 200 Mrad) gives an ENDOR spectrum which is a singlet centered at 14.4 MHz [51] (Fig. 3). This ENDOR spectrum provides substantial proof for the formation of polyenyl radicals and extensive delocalization of the unpaired electrons in irradiated PVC samples.

The decay of free radicals formed in irradiated PVC has been investigated by several authors [4, 20, 51, 52]. A relation between radical decay and color formation has been found [4, 20]. In a study of the radical decay in an irradiated PVC sample three types of radicals with different half-lives were separated (Table 1) and attributed to polyene radicals with different number of conjugated double bonds [4].

It has been found [53] that PVC acts as an electron scavenger to produce primary PVC radicals in $\gamma$-irradiated PVC-MTHF (methyltetrahydrofuran) glass. The dissociative electron capture plays an important role in the formation of the primary PVC radical in the above system.

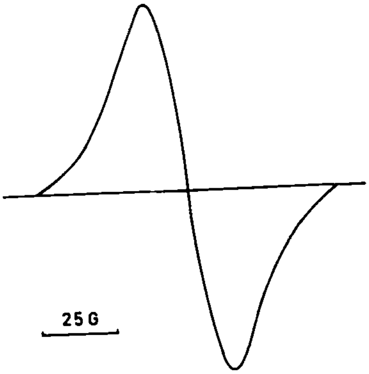


FIG. 2. ESR spectrum of $\gamma$-irradiated poly(vinyl chloride) at room temperature [22].

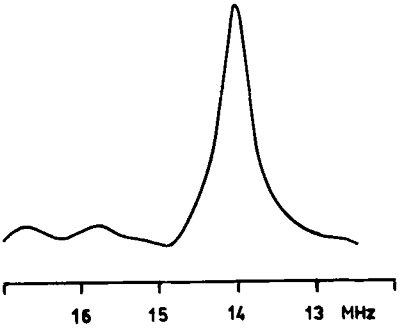


FIG. 3. Matrix ENDOR spectrum of $\gamma$-irradiated poly(vinyl chloride) [51].

TABLE 1. Half-life of Different Radical Species Obtained from Radical Decay Curves[a]

| | At 80°C | At 55°C | At 30°C |
|---|---|---|---|
| Short-lived (min) | 20 | 40 | 54 |
| Long-lived (min) | 210 | 400 | 720 |
| Very long-lived (hr) | 135 | 141 | 3200 |

[a] Data of Atchison [4].

During $\gamma$-irradiation of PVC in the absence of oxygen at -196°C, alkyl radicals are formed. When exposed to air, these radicals are transformed to peroxy radicals. This reaction can be followed by ESR [42]. When the sample is exposed to air at -78°C, the peroxy radical concentration reaches a maximum after 100 min exposure time. The peroxy radical formation is diffusion-controlled. At higher temperatures the rate of peroxy radical formation is so high that it is not easily followed by ESR. After evacuation of the sample the peroxy radical concentration decreased exponentially with a simultaneous increase in the alkyl radical concentration until virtually all radicals were in the alkyl form. Several reaction schemes have been proposed to explain the reversibility of the alkyl radical disappearance. The reactions (17)-(20) seem to be the most reasonable:

$R\cdot + O_2 \longrightarrow RO_2\cdot$ (fast reaction) (17)

$RO_2\cdot + R'H \longrightarrow ROOH + R'\cdot$ (18)

$R'\cdot + O_2 \longrightarrow R'O_2\cdot$ (fast reaction) (19)

$2R'\cdot \longrightarrow$ non-radical products (fast reaction) (20)

## ESR STUDY OF PHOTODECOMPOSITION OF PVC

Only a few papers report on ESR spectra obtained during UV irradiation of PVC [54-57]. The ESR spectrum of PVC UV-irradiated at -196°C consists of a single line containing an apparent broad and a narrow component, e.g., two overlapping signals [57] (Fig. 4). The broad component of the ESR spectrum can be attributed to some kind of alkyl radicals and the narrow component to polyenyl radicals. The ESR spectra formed during UV irradiation at -196°C are not significantly influenced by the presence or absence of oxygen. The decay curves (Fig. 5 and 6), however, differ, depending on the conditions for irradiation of the PVC samples. The results show that the unresolved single line spectrum obtained for PVC (UV-irradiated in air) cannot be related only to the formation of polyene structures. Formation and disappearance of typical peroxy radical spectra for PVC was observed (Fig. 6). Polyene radicals produce a symmetrical and peroxy radicals an asymmetrical ESR spectrum. These spectra are overlapping and difficult to completely separate. Thus the decay curve in Fig. 6 attributed to peroxy radicals may to some extent contain contributions from the decay of the polyene radicals present.

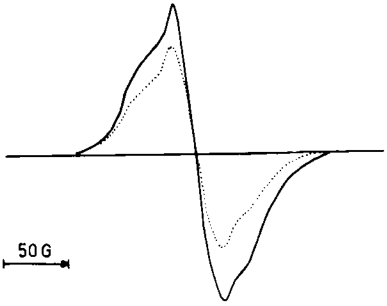


FIG. 4. ESR spectra of UV-irradiated poly(vinyl chloride) at -196°C: (•••) in vacuo; (—) in air.

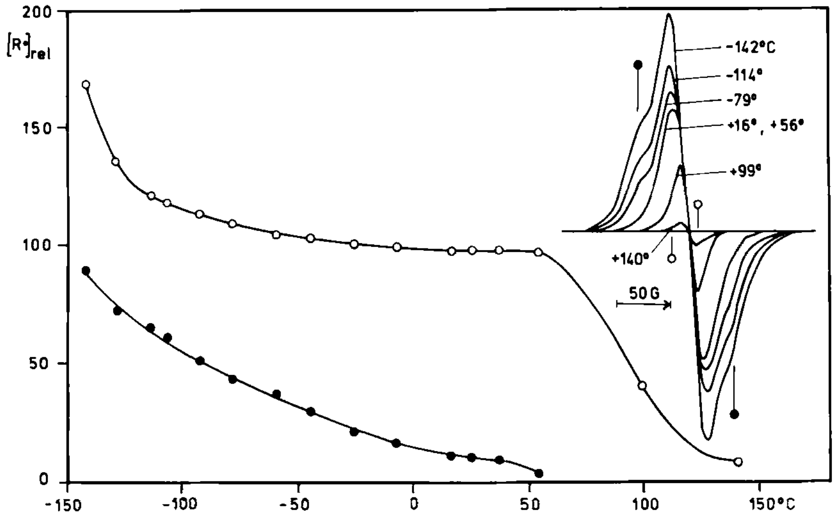


FIG. 5. Changes of ESR spectra and kinetics of decay of free radicals in the poly(vinyl chloride) sample UV-irradiated in vacuo during heating: ( ● ) attributed to alkyl radical decay; ( ○ ) attributed to polyenyl radical decay.

Pure PVC does not absorb UV light of wavelengths longer than 190 nm. Measurements of ultraviolet absorption spectra of PVC films show a rapidly increasing absorption below 220 nm and a low intensity absorption ( $< 0.1$) even up to 320 nm [58]. This fact and the observation that free radicals are formed after UV irradiation at a wavelength 254 nm in vacuo indicate the presence of some type of

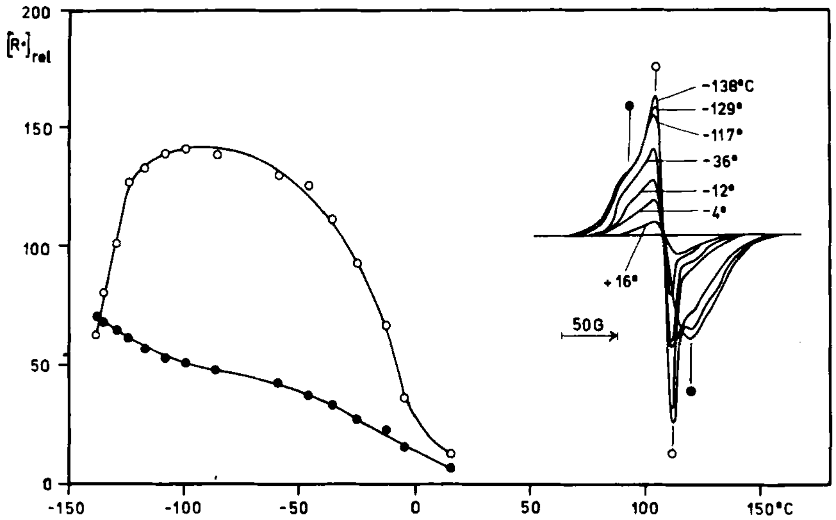
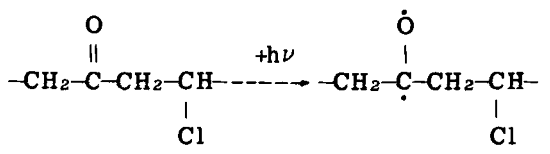


FIG. 6. Changes of ESR spectra and kinetics of decay of free radicals in the poly(vinyl chloride) sample UV-irradiated in vacuo after including air and heating: ( ● ) attributed to alkyl radical; ( ○ ) attributed to formation and decay of peroxy radicals (may also include the decay of polyenyl radicals).

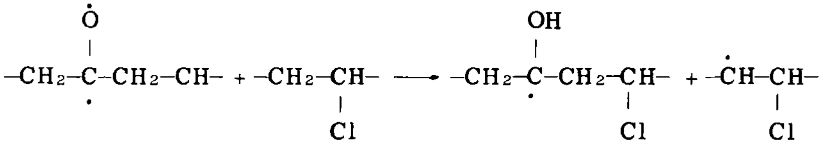
chromophores. Also small quantities of external impurities may be responsible for the absorption of light quanta above 190 nm. The most probable chromophores present in PVC are double bonds distributed at random and a small amount of carbonyl groups which may have formed during the polymerization process.

Small amounts of carbonyl groups (e.g., 1 carbonyl group for 100-1000 mers) could be responsible for a photoinitiation process which is described by the following reactions.



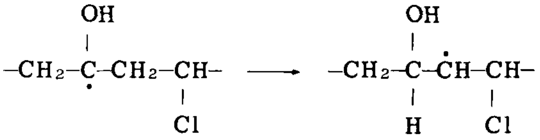
$$-CH_2-\overset{\overset{\Large O}{\|}}{C}-CH_2-\underset{\underset{\Large Cl}{|}}{CH}- \xrightarrow{+h\nu} -CH_2-\underset{\bullet}{\overset{\overset{\Large \dot{O}}{|}}{C}}-CH_2-\underset{\underset{\Large Cl}{|}}{CH}- \qquad (21)$$

In this way the first stage is the excitation of a carbonyl group by UV light to its triplet state which is a biradical. It is well known that carbonyl groups in triplet state may easily abstract hydrogen atoms from neighboring molecules [Eq. (22)].



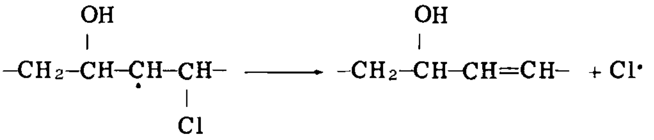
$$-CH_2-\underset{\bullet}{\overset{\overset{\bullet}{O}}{C}}-CH_2-CH- + -CH_2-\underset{Cl}{CH}- \longrightarrow -CH_2-\underset{\bullet}{\overset{OH}{C}}-CH_2-\underset{Cl}{CH}- + -\overset{\bullet}{C}H-\underset{Cl}{CH}- \qquad (22)$$

Assuming an exchange between an unpaired electron and a neighboring hydrogen (a hydrogen transfer) we can write Eq. (23).



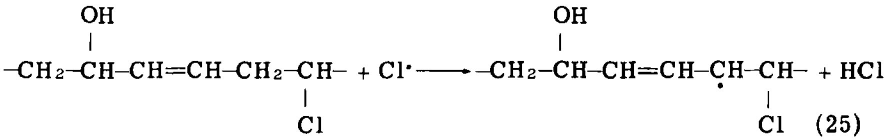
$$-CH_2-\underset{\bullet}{\overset{OH}{C}}-CH_2-\underset{Cl}{CH}- \longrightarrow -CH_2-\underset{H}{\overset{OH}{C}}-\overset{\bullet}{C}H-\underset{Cl}{CH}- \qquad (23)$$

The presently available evidence [59] indicates that when an unpaired electron is formed in beta-position to a halogen atom, a halogen radical is expelled and a double bond is formed [Eq. (24)].



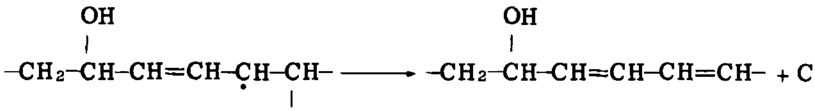
$$-CH_2-\overset{OH}{CH}-\underset{\bullet}{C}H-\underset{Cl}{CH}- \longrightarrow -CH_2-\overset{OH}{CH}-CH{=}CH- + Cl\cdot \qquad (24)$$

The relative reactivity of C–H bonds towards chlorine radicals can be expressed as: primary C–H=1, secondary C–H = 3.6, and tertiary C–H = 4.2 [60]. Hydrogen abstraction from a methylene group ($-CH_2-$) is more probable than the abstraction of tertiary bonded hydrogen from a $-CH(Cl)-$ group due to polar effects. Measurements indicate that hydrogen abstraction from methane by chlorine free radicals occurs much more easily ($E_a$ = 1.0 kcal/mole) than from chlorinated methane ($E_a$ = 5.5 kcal/mole) [61]. For that reason the chlorine formed in reaction (4) abstract hydrogen atoms from methylene groups ($-CH_2-$) preferentially. Abstraction from tertiary ($-CH(Cl)-$) groups may occur but at a lower rate.



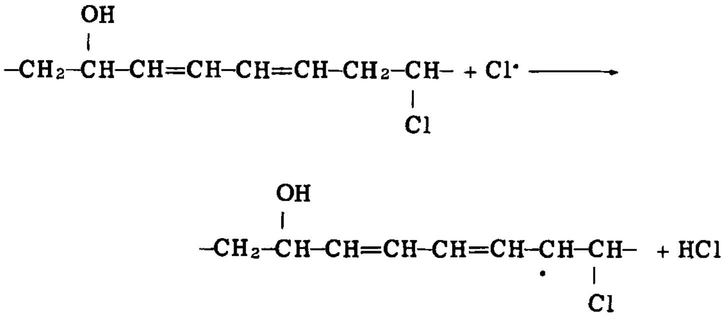
$$-CH_2-\overset{OH}{CH}-CH{=}CH-CH_2-\underset{Cl}{CH}- + Cl\cdot \longrightarrow -CH_2-\overset{OH}{CH}-CH{=}CH-\underset{\bullet}{C}H-\underset{Cl}{CH}- + HCl \qquad (25)$$

Further reactions are analogous and mean a repetition of the reactions (24) and (25):



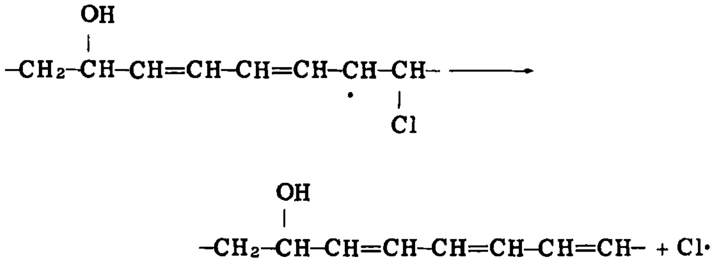
$$-CH_2-\overset{OH}{\overset{|}{C}H}-CH=CH-\underset{\bullet}{C}H-\underset{\underset{Cl}{|}}{C}H- \longrightarrow -CH_2-\overset{OH}{\overset{|}{C}H}-CH=CH-CH=CH- + Cl\cdot$$

(26)



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

(29)

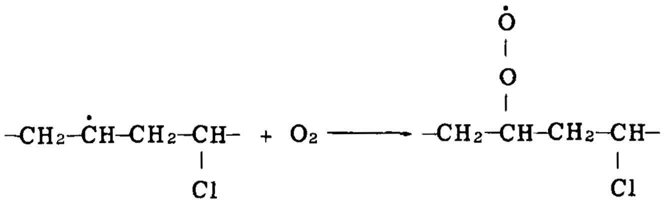


$$-CH_2-\overset{OH}{\overset{|}{C}H}-CH=CH-CH=CH-\underset{\bullet}{C}H-\underset{\underset{Cl}{|}}{C}H- \longrightarrow -CH_2-\overset{OH}{\overset{|}{C}H}-CH=CH-CH=CH-CH=CH- + Cl\cdot$$

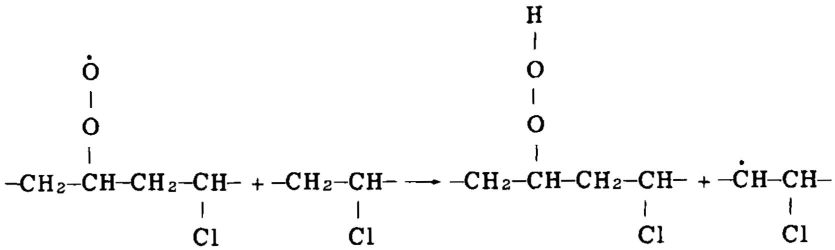
(28)

This mechanism explains well the rapid formation of conjugated double bonds and of polyenyl radicals observed by ESR spectroscopy during UV irradiation of PVC in vacuo. Studies of PVC samples with different syndiotacticities, UV-degraded at temperatures between 10 and 115°C, show that the average number of conjugated double bonds formed in sequence increases with increase in syndiotacticity of PVC [62].

In the presence of oxygen, peroxy radicals are formed rapidly and this reaction in the solid state is diffusion-controlled. Hydroperoxide groups can only be formed in the presence of air by addition of molecular oxygen to macroradicals:

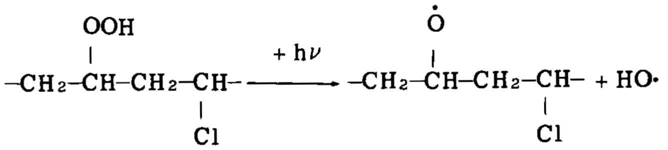


$$-\mathrm{CH_2}-\overset{\bullet}{\mathrm{C}}\mathrm{H}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}- \; + \; \mathrm{O_2} \longrightarrow -\mathrm{CH_2}-\overset{\overset{\overset{\overset{\bullet}{\mathrm{O}}}{|}}{\overset{\mathrm{O}}{|}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}- \qquad (29)$$



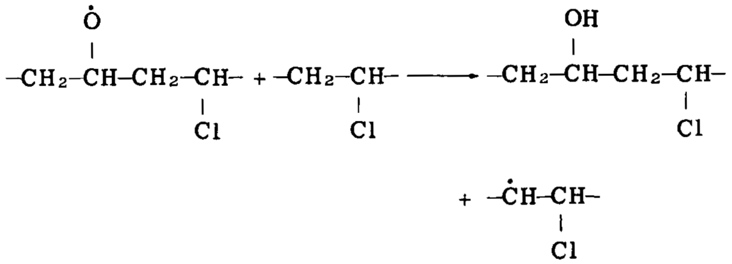
$$-\mathrm{CH_2}-\overset{\overset{\overset{\overset{\bullet}{\mathrm{O}}}{|}}{\overset{\mathrm{O}}{|}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}- \; + \; -\mathrm{CH_2}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}- \longrightarrow -\mathrm{CH_2}-\overset{\overset{\overset{\overset{\overset{\mathrm{H}}{|}}{\mathrm{O}}}{|}}{\overset{\mathrm{O}}{|}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}- \; + \; -\overset{\bullet}{\mathrm{C}}\mathrm{H}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}- \qquad (30)$$

On the other hand, the UV light quanta of the wavelength 254 nm have enough energy to easily photodissociate hydroperoxide bonds: CO–OH (42 kcal/mole), C–OOH (70 kcal/mole) [63]. The great difference in bond dissociation energy between CO–OH and C–OOH means that reaction (31) is predominant in the photolysis with UV [Eq. (31)].



$$-\mathrm{CH_2}-\overset{\overset{\mathrm{OOH}}{|}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}- \xrightarrow{+h\nu} -\mathrm{CH_2}-\overset{\overset{\overset{\bullet}{\mathrm{O}}}{|}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}- \; + \; \mathrm{HO}\cdot \qquad (31)$$

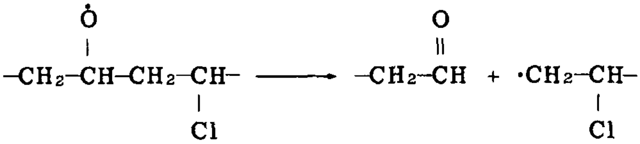
Oxy-radicals are very reactive. They abstract hydrogen easily from neighboring macromolecules [Eq. (32)].



$$-\mathrm{CH_2}-\overset{\overset{\overset{\bullet}{\mathrm{O}}}{|}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}- \; + \; -\mathrm{CH_2}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}- \longrightarrow -\mathrm{CH_2}-\overset{\overset{\mathrm{OH}}{|}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}- \; + \; -\overset{\bullet}{\mathrm{C}}\mathrm{H}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}- \qquad (32)$$

For this reason it is expected that the observed IR absorption in the range 3500-3000 $cm^{-1}$ refers mainly to the hydroxyl groups formed.

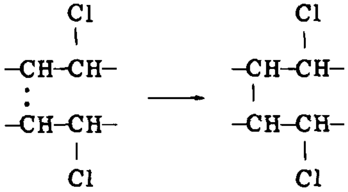
After long time of UV irradiation (20 hr) in the presence of air, a low intensity IR absorption peak due to carbonyl groups is formed at 1740 $cm^{-1}$. This is probably the result of the reaction (33).



$$-CH_2-\overset{\overset{\dot{O}}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}- \longrightarrow -CH_2-\overset{\overset{O}{\|}}{CH} + \cdot CH_2-\underset{\underset{Cl}{|}}{CH}- \qquad (33)$$

This reaction plays an important part in the scission of the polymer chains.

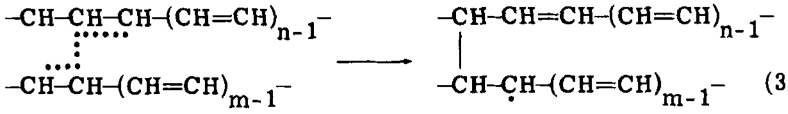
It has been found that scission and crosslinking occur simultaneously in the same irradiated polymer sample. The gel content varies very much from 20 to 50%, depending on UV irradiation, and it is not reproducible. According to the general opinion, crosslinking in vacuo occurs by the coupling of two macroradicals [Eq. (34)].



$$\begin{array}{l} \overset{\overset{Cl}{|}}{-CH}-CH- \\ \;\vdots \\ -CH-\underset{\underset{Cl}{|}}{CH}- \end{array} \longrightarrow \begin{array}{l} \overset{\overset{Cl}{|}}{-CH}-CH- \\ \;| \\ -CH-\underset{\underset{Cl}{|}}{CH}- \end{array} \qquad (34)$$

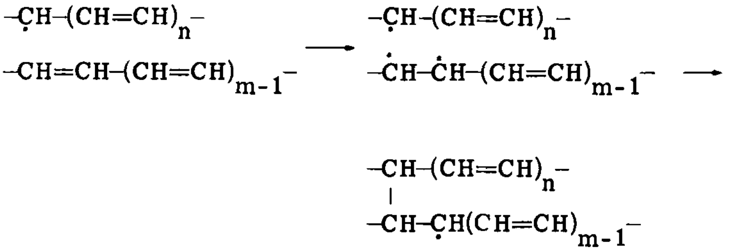
This type of reaction occurs at elevated temperatures when the macroradicals have enough mobility for this type of termination.

We may suggest as possible that the delocalization of unpaired electron can also occur intermolecularly between two macromolecules having conjugated double bond sequences in which the electron clouds partially overlap [Eq. (35)].



$$\begin{array}{l} -CH-\underset{\cdots\cdots}{CH}-CH-(CH{=}CH)_{n-1}- \\ \;\vdots \\ -CH-CH-(CH{=}CH)_{m-1}- \end{array} \longrightarrow \begin{array}{l} -CH-CH{=}CH-(CH{=}CH)_{n-1}- \\ \;| \\ -CH-\underset{\bullet}{CH}-(CH{=}CH)_{m-1}- \end{array} \qquad (35)$$

or when one of the double bonds is excited to the triplet state by absorption of light:



$$\begin{matrix}-\underset{\cdot}{C}H-(CH=CH)_n- \\ -CH=CH-(CH=CH)_{m-1}-\end{matrix} \longrightarrow \begin{matrix}-\underset{\cdot}{C}H-(CH=CH)_n- \\ -\dot{C}H-\dot{C}H-(CH=CH)_{m-1}-\end{matrix} \longrightarrow \begin{matrix}-CH-(CH=CH)_n- \\ | \\ -CH-\underset{\cdot}{C}H(CH=CH)_{m-1}-\end{matrix} \qquad (36)$$

In both these reactions (35) and (36) crosslinking is caused by an intermolecular electron delocalization between the two polyene structures. If this type of reaction occurs, we should observe crosslinking reaction even at -196°C without changes in the single line ESR spectrum. It is difficult to prove these reactions experimentally, because there is no method yet available for determination of the number of crosslinks at low temperatures.

## ESR STUDIES OF CHEMICAL DECOMPOSITION OF PVC

Also PVC samples extensively dehydrohalogenated by the reaction with alkali amides [54] show a single-line ESR signal with a half-width value 7-12 G, which was assigned to unpaired electrons delocalized in long chains of conjugated double bonds.

## CONCLUSIONS

The following conclusions may be drawn from the ESR studies of the different PVC decomposition mechanisms presented here.

(1) It is difficult to verify the presence of alkyl and allyl polymer radicals at room or elevated temperatures.

(2) The fact that alkyl and allyl polymer radicals are not observable during decomposition at room temperature of PVC is not adequate proof for the reaction to occur by ionic mechanism. The concentration and lifetime of these radicals at room or elevated temperatures may be too small for their detection by ESR.

(3) The single-line ESR spectra observed in all methods of decomposition of PVC can be attributed to unpaired electrons delocalized along conjugated double bond systems (polyene radicals). This delocalization is responsible for the high stability of polyene radicals even at high temperatures.

(4) The number of double bonds in the conjugated system delocalizing the electron influences the ESR spectra (the width of the single line) from the polyenyl radicals.

(5) Formation of semiaromatic structures during thermal decomposition of PVC increases the stability of the delocalized unpaired electron in PVC and gives semiconducting properties to the samples [64]. The ESR spectra of samples pyrolyzed above 400°C have been attributed to delocalization of free electrons in cycloaromatic structures.

(6) The presence of delocalized electrons in PVC samples containing polyene structures shows that the decomposition occurs by a free radical mechanism. There is no reasonable explanation for the formation of unpaired electrons in a purely ionic mechanism. Radical-ionic mechanism, e.g., one electron transfer can be acceptable.

(7) The role of oxygen in the formation of free radicals is still controversial. There is some difficulty in distinguishing between alkyl peroxy (ROO•) and alkoxy (RO•) radicals since both have the unpaired electron mainly centered on oxygen atoms and both give singlet spectra with no hyperfine interaction with alkyl protons [65].

In the presence of polyenyl radicals, which probably are not reactive enough to attack molecular oxygen, ESR spectra of three different radicals may overlap, which further complicates the interpretation.

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## DISCUSSION

Dr. Favre (France): In his paper Prof. Rånby said that carbonate groups are responsible for the initiation of degradation of PVC. Does he think that Norrish scission is possible in PVC chains, can he explain it?

Prof. Rånby: Norrish scission is possible there, but it is less likely on the chains containing chlorine atoms. I have outlined the possibility of having a reaction which leads to hydroxyl groups. At present we have great difficulty in finding a mechanism which gives us hydroxyl groups on the chains. If carbonyl groups are present, they will absorb the light up to about 310 nm or 320 nm, which means that they could form even in sunlight. As I also pointed out, there is a difficulty in understanding what starts the reaction. This is because there are certain groups on the PVC chain which absorb the light and start the reaction, but there are a few of them and they can react in different ways, which I explained too.

Dr. Wirth (Ciba-Geigy, Marienberg, West Germany): What is Prof. Rånby's opinion on the implication of singlet oxygen on the light degradation of PVC? Secondly, is there no Norrish type I reaction to be considered in the degradation of PVC to explain the chain scissions?

Prof. Rånby: It is quite possible that there are singlet oxygen reactions in PVC, but this has not yet been established. We are afraid, however, that the rather complex thermal stabilizers which are now available, including these organotin compounds, may be activated by ultraviolet light because, if they are, they would then transfer to oxygen. That is one reaction which has to be considered; we do not yet know to what extent it would be active. In this respect, there is a second point–which I mentioned only briefly–that it is not necessarily the case that the tin mercapto-organic compounds are only substituting. If they are split by UV light, they would form a sulfur radical which could abstract chlorine, thus leaving a radical on the chain. Of course, this would be extremely unfortunate, since then it would not necessarily have to be substituted, but the radical on the chain could continue the process by being oxidized. About the Norrish type I and II reactions on PVC, these cannot be excluded, but it is difficult to distinguish one of these reactions from other possibilities. I described one type of reaction undergone by the alkoxy radical on the chain which also gave a scission, but that is not a Norrish type I but a $\beta$-scission.

It is surprising that there is so little chain scission in the initial phases of the PVC photodecomposition. It has to be carried further on, when there are many groups and many possible reactions, before there is any significant amount of degradation. It should be mentioned that before this significant amount of degradation occurs, there is considerable crosslinking. If there are radicals formed on the PVC chains which are in conjunction with polyene structures, these are mobile because the free electrons are actually delocalized within the whole sequence. This means that two chains can meet at many points, so that there is a greatly increased probability of crosslinking. That is a type of reaction which has not been discussed at this meeting and it is important because this type of crosslinking inevitably produces a more brittle material. Brittleness is a detrimental feature with respect to the photostability of a material.

Dr. G. C. Marks (BP Chemicals, Sully, South Wales, U. K.): I should like to ask Prof. Rånby about the sample form used in his experiments. I am particularly concerned with his view regarding the role of carbonyl groups in the initiation step. If, for example, his samples were prepared by thermal processing, I would have thought that conjugated carbon-carbon sequences would be much more likely to be initiation sources. Alternatively, if the samples were, say, cast from solution, what precautions were taken to avoid contamination, hydroperoxidation or even carbonyl formation from that source?

Prof. Rånby: The samples we have used are prepared by thermal calendering–the sort of method used for the introduction of stabilizer to obtain a homogeneous sheet. We have also made castings, but I have not reported these here. From these we have demonstrated that it is dangerous to introduce a solvent because, for instance, as little as 1% of tetrahydrofuran remaining in the PVC is extremely detrimental and would cause considerable confusion in the photochemical experiments. Thus, we try to avoid solutions. Of course, if solutions from casting are avoided, we have to go to high temperatures in order to introduce the stabilizer system homogeneously. Thus, it is possible that we do introduce this type of group in the processing of our samples. This is described in my paper.