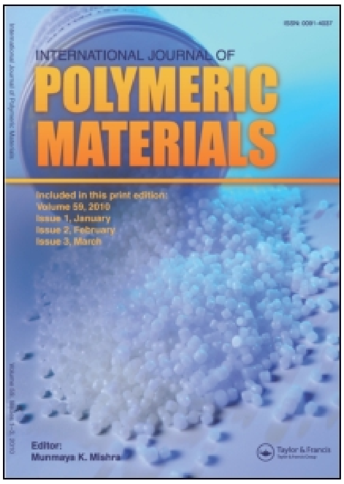

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Behnisch, J. and Zimmermann, H.(1992) 'Kinetics and Mechanism of the Polyene Formation during Dehydrochlorination of Poly(Vinyl Chloride) in the Solid State', International Journal of Polymeric Materials, 16: 1, 143 — 157

To link to this Article: DOI: 10.1080/00914039208035417

URL: http://dx.doi.org/10.1080/00914039208035417

Intern. J. Polymeric Mater., 1992, Vol. 16, pp. 143–157
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Printed in the United Kingdom

Kinetics and Mechanism of the Polyene Formation during Dehydrochlorination of Poly(Vinyl Chloride) in the Solid State

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In investigating the thermal, photolytical and chemical dehydrochlorination of poly(vinyl chloride) (PVC) it is shown that the formation of polyenes proceeds independently of the kind of initiation in a fast zip reaction and by the same mechanism. The sequence length distribution of the formed polyenes depends mainly on the conformation of the PVC chains. A strong correlation between this distribution and the conformation equilibrium of the polymer chains as well as the physical structure of the polymer solid is demonstrated.

KEY WORDS Dehydrochlorination, PVC, kinetics, mechanism

Results and Discussion

During the last decade much of the attention in the field of poly(vinyl chloride) (PVC) degradation has been paid to the reactions initiating the dehydrochlorination and therefore the formation of conjugated double bonds, and only relatively little attention has been paid to the study of the polyene growth itself. In this paper we summarize in two main theses the results of our investigations on the kinetics and the mechanism of polyene formation during thermal, photolytical and chemical degradation of PVC. Besides the practical interest in PVC stability, the main goal of our fundamental research is to study a macromolecular reaction in detail, and particularly to answer the question of how the physical state of the polymer matrix influences such a reaction.

First we give a brief introduction to the background of knowledge on the three degradation reactions. Figure 1 shows the polyene absorption at different degrees of thermal dehydrochlorination. As will be seen, even at very low conversions a complete distribution of the sequence length of the polyenes is obtained which does not change during further dehydrochlorination. Thus, polyene formation proceeds not step-by-step, but in a so-called zip reaction with three elementary steps: initiation, propagation and termination. As the mechanism of the polyene formation during thermal degradation, now the ion-pair mechanism, proposed by

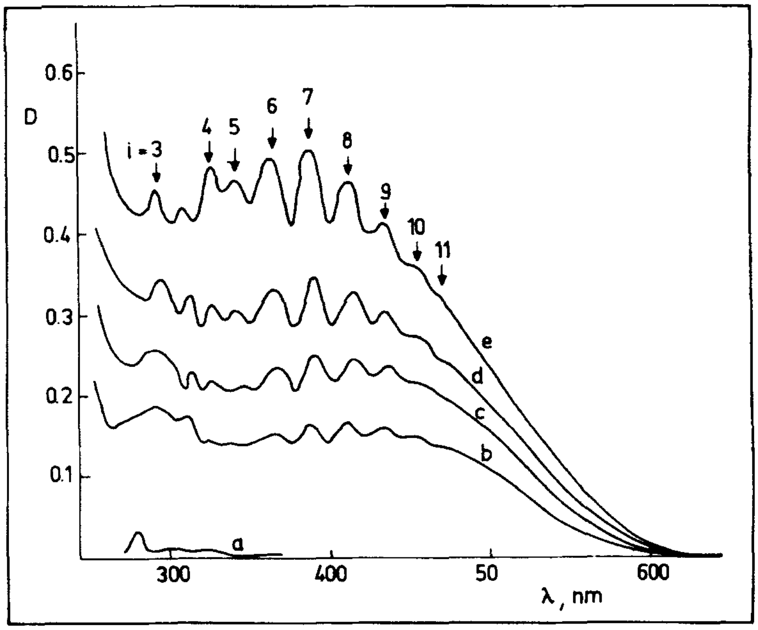
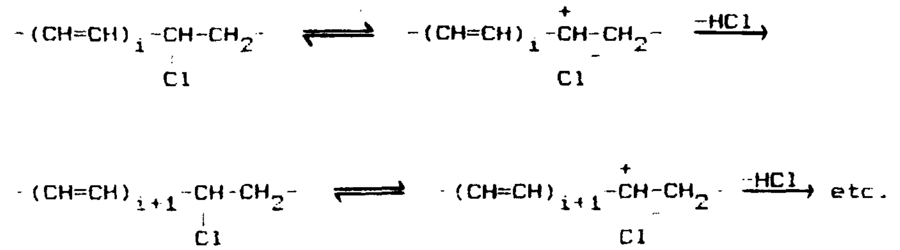


FIGURE 1 UV-VIS-spectra of poly(vinyl chloride) degraded at 180°C up to a degree of dehydrochlorination of α = 0.05%, 0.1% and 0.3%.



$$-(CH{=}CH)_i-\underset{Cl}{CH}-CH_2- \rightleftharpoons -(CH{=}CH)_i-\overset{+}{\underset{Cl}{CH}}-CH_2- \xrightarrow{-HCl}$$

$$-(CH{=}CH)_{i+1}-\underset{Cl}{CH}-CH_2- \rightleftharpoons -(CH{=}CH)_{i+1}-\overset{+}{\underset{Cl}{CH}}-CH_2- \xrightarrow{-HCl} \text{etc.}$$

FIGURE 2 Ion-pair mechanism of the polyene growth during thermal degradation of poly(vinyl chloride) (W. H. Starnes, Jr., Developments in Polymer Degradation, Vol. 3, N. Grassie, ed., Applied Science Publishers, London, 1981, p. 135).

Starnes[1] and shown in Figure 2 is widely accepted. The main idea of this mechanism is an increased polarization and even ionization of the C–Cl bond in β-position to a double bond, thus favoring the abstraction of a hydrogen atom from the next methylene group.

Polyenes are formed immediately in the case of photodegradation of PVC also, and even at room temperature (see Figure 3). A widely accepted mechanism of the photodegradation of PVC is proposed by Decker[2] (Figure 4). According to it, only initiation is activated by light, whereas the polyene growth is a thermally activated radicalic zip reaction.

According to the reaction scheme proposed by Wirsen and Flodin,[3] polyenes are formed in a step-by-step E2-elimination reaction in the case of chemical degradation of PVC (Figure 5). Therefore, a kinetic behavior different from that in the case

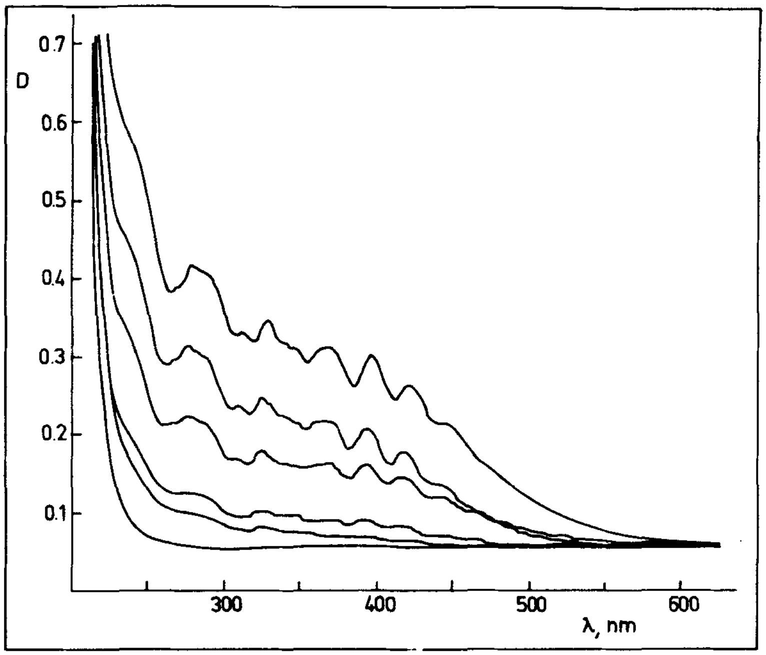


FIGURE 3 UV-VIS-spectra of a poly(vinyl chloride) film (50 μm, cast from 1,2-DCE) photodegraded ($\lambda = 254$ nm) at 25°C ($t = 0$, 10, 15, 30, 45, and 60 min).

of thermal and photolytical dehydrochlorination must be proposed. However, as our investigations show (Figure 6), this is not valid: even during chemical dehydrochlorination of PVC, longer polyenes are formed immediately and their sequence length distribution changes only slightly with reaction time. Summarizing this introduction we see that for all three kinds of degradation a special chemical and kinetic mechanism of the polyene formation is assumed in the literature.

But in our opinion, and this should be the *first thesis: The formation of polyenes proceeds by the same mechanism, probably the ion-pair mechanism already mentioned, independent of the type of initiation or in other words, independent of the type of formation of the first double bond.*

This thesis is supported at least by two experimental results. (1) The sequence length distribution of polyenes formed in the same PVC film at the same temperature degraded to the same degree of dehydrochlorination is quite similar in the cases of photodegradation and chemical degradation (see Figure 7), as we proposed in our thesis. (2) As a consequence of this thesis the propagation of polyene formation must proceed much faster than the initiation reaction, which means the following relationship must be valid:

$$k_0 << k_p.$$

Proving this relationship was difficult because no values of k_p exist in the literature. However, a careful kinetic analysis of the induction period of the formation of

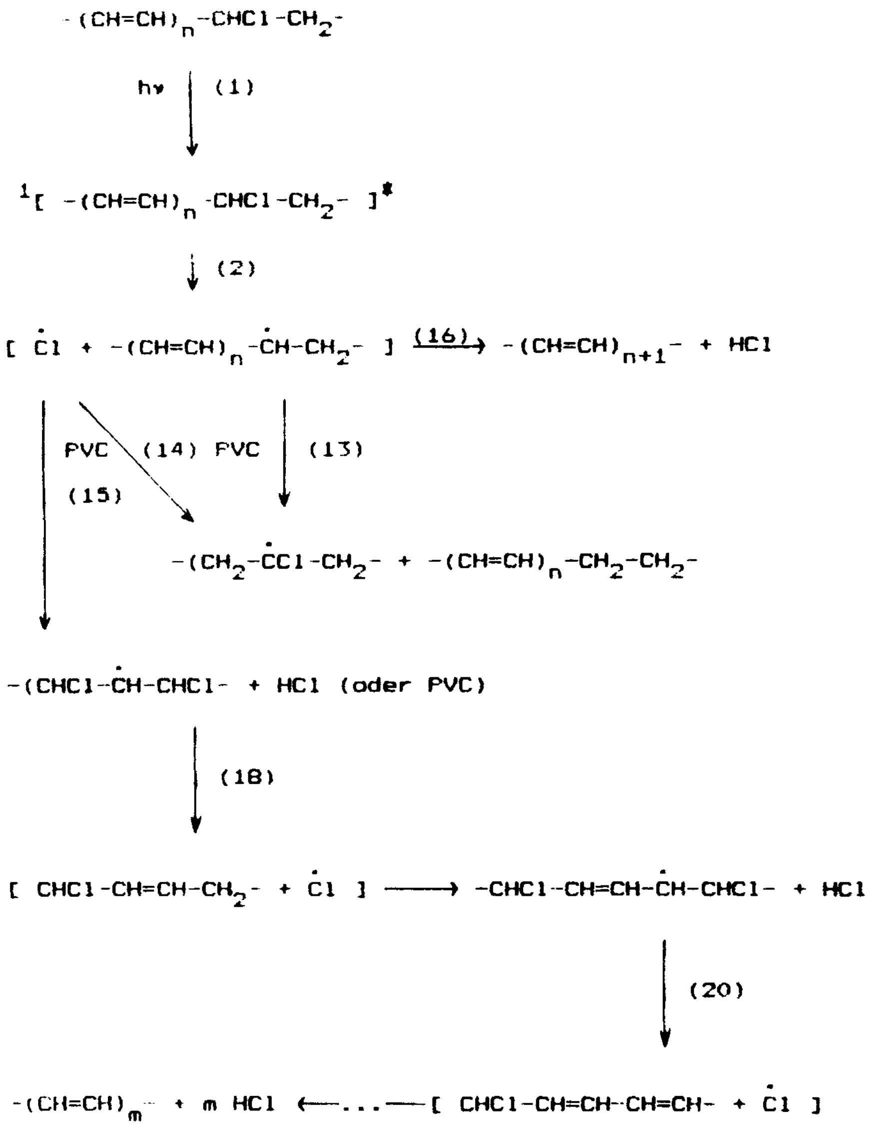


FIGURE 4 Mechanism of initiation and propagation of polyene formation during photodegradation of poly(vinyl chloride) (C. Decker, Photodegradation of PVC, in Degradation and Stabilisation of PVC, E. D. Owen, ed., Elsevier Applied Science Publishers, London, New York, 1984).

polyenes of different sequence length enables us, for the first time, to estimate the rate constant k_p.

In Figure 8 these results are shown together with the rate constant of initiation in the case of thermal degradation (at normal PVC sites k_0, and at defect structures k_F) and in the case of photolytical (*) and chemical (O) initiation: in all cases propagation proceeds faster by several orders of magnitude and the relationships $k_0 << k_p$ is in fact valid.

According to our thesis, we propose the following modification of the reaction

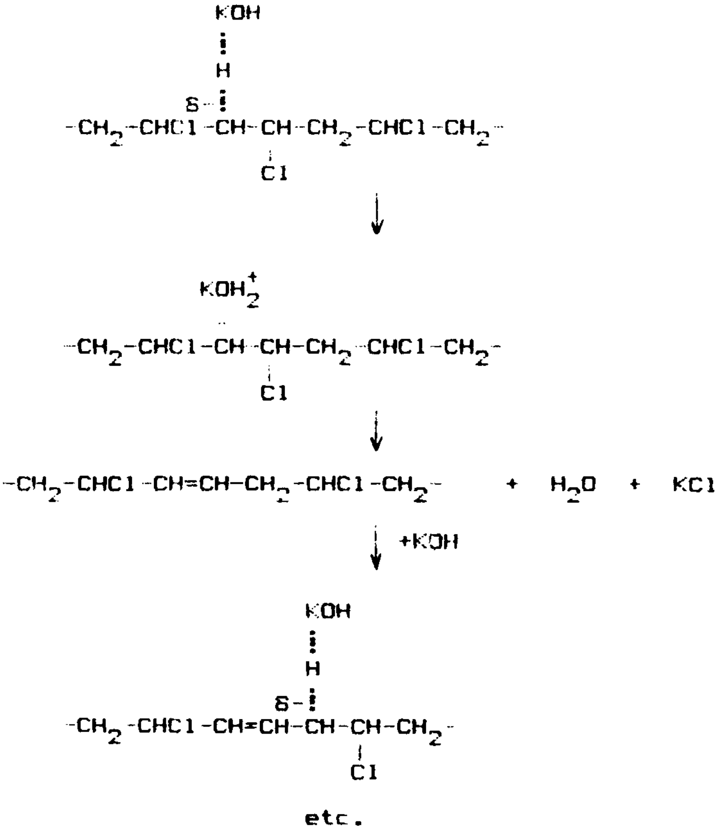


FIGURE 5 Mechanism of initiation and propagation of polyene formation during chemical dehydrochlorination of poly(vinyl chloride) by KOH (A. Wirsen and P. Flodin, *J. Appl. Polym. Sci.*, **22**, 3039 (1978).

schemes. In the case of photodegradation (see Figure 9) it is identical to the above-mentioned scheme, including the formation of the first double bond (Figure 4), but then we suggest that the cage is left (reaction step (21)) and the chlor-radical transfers to another segment of the PVC chain, whereas the polyene growth proceeds by the ion-pair mechanism (step (22)).

In the case of chemical degradation (see Figure 10) the first double bond is formed by the above-mentioned E2-elimination but is followed by polarization of the C–Cl bond in the β-position and by fast polyene growth according to the ion-pair mechanism. It is worthwhile to note that this thermally activated polyene propagation goes in a direction opposite to the proposed E2-elimination polyene growth, which means that both propagation reactions could proceed at the same time but with different rate constants in favor of the thermal propagation.

Our second main thesis deals with an old problem in PVC degradation still under discussion. Why does polyene formation proceed so fast even in the solid state and quite below the glass-transition temperature and why does it stop, thus leading to polyenes of different and limited sequence length?

In our opinion, Millan and coworkers[4] answered this question in 1973 when they

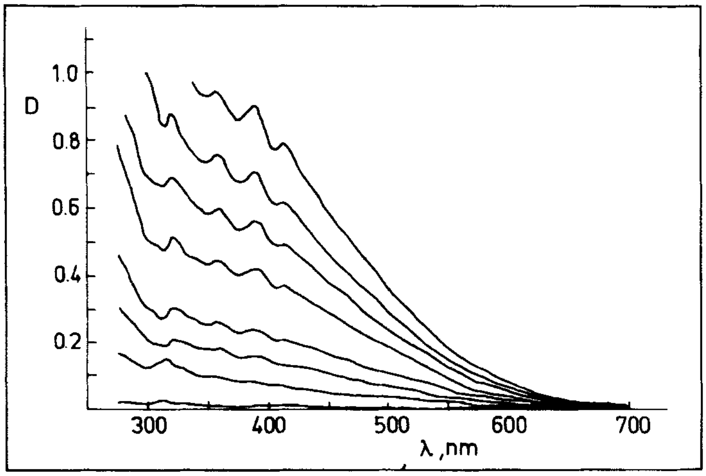


FIGURE 6 UV/VIS-spectra obtained in situ during chemical degradation of a poly(vinyl chloride) film by KOH in water using a phase transfer agent (TEAB) at t = 0, 30, 70, 105, 145, 215, 250 and 300 min.

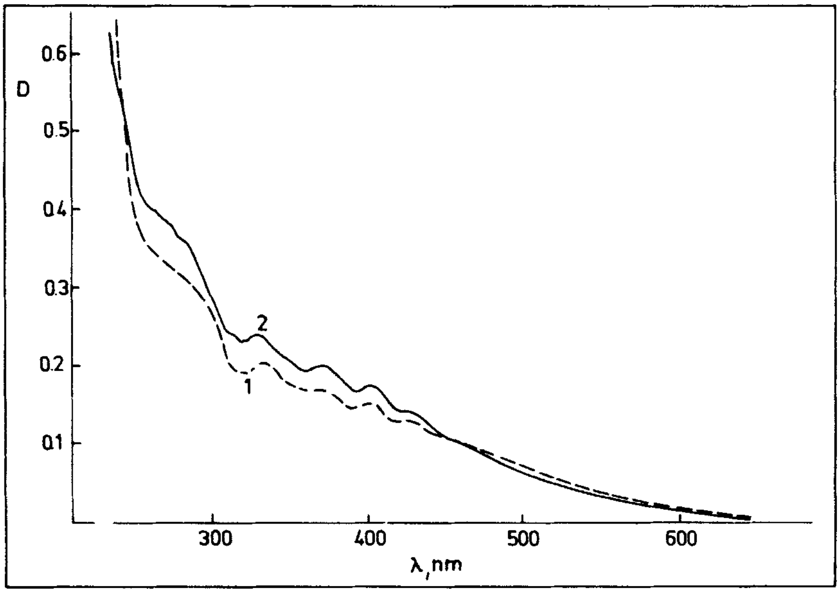


FIGURE 7 Comparison of the uv-VIS-spectra of poly(vinyl chloride) films (50 μm, cast from 1,2-DCE) degraded at 25°C to the same degree of dehydrochlorination (about 0.5%) (1) by photoinitiation (254 nm) and (2) initiated by chemical dehydrochlorination with KOH in water (using TEAB).

showed that PVC with higher syndiotacticity forms easily longer polyene sequences during thermal degradation. It is surprising that the influence of tacticity is often mentioned in the literature, but not completely accepted and verified. However, in our opinion, and this is the *second thesis: The conformation of the PVC macromolecules is the main factor influencing the formation of polyenes and their sequence length distribution.*

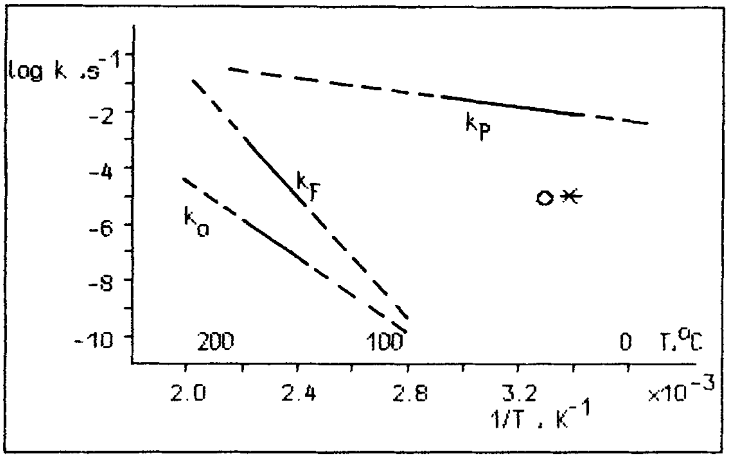


FIGURE 8 Rate constants of propagation K_p and initiation; K_0 is the thermal degradation; K_f are the defect structures; * indicates photolytical and O chemical.

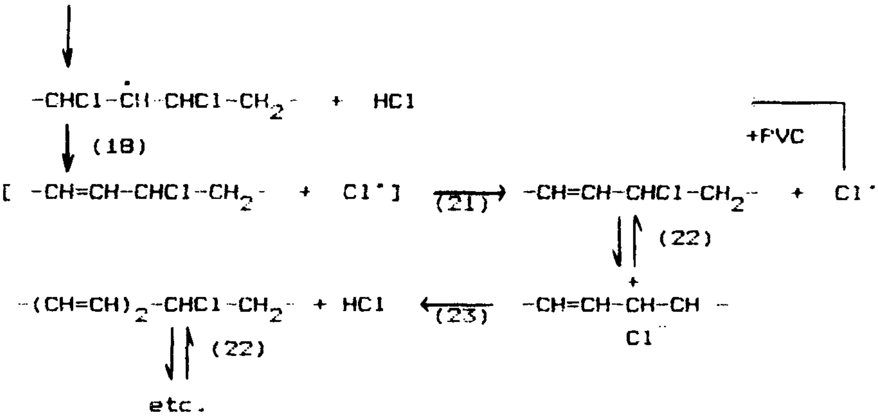


FIGURE 9 Modified reaction scheme of the thermally activated polyene growth by the ion-pair mechanism during photodegradation of poly(vinyl chloride).

To explain this, we compare the geometry of the C–C backbone of the most probable conformation of syndiotactic PVC sequences and of trans-polyacetylene (see Figure 11). As can be seen from Figure 11, only a small rearrangement of the C–C backbone is necessary during dehydrochlorination. Obviously, the syndiotactic all-trans conformers of PVC for steric reasons are ideal precursors for the formation of all-trans polyenes and this is the main explanation as to why the polyene formation proceeds so fast even in the solid state. By the same reason any deviation from that all-trans conformer, as it is, e.g., a gauche-conformer, needs additional rearrangmeents of the main chain and favors termination of the polyene growth. Therefore, discussing the distribution of the conformations of a PVC-triade and using the rule that a trans-conformation element means propagation and gauche-element leads to termination, we are able to predict the termination structures of polyenes and their relative contents (see Table I).

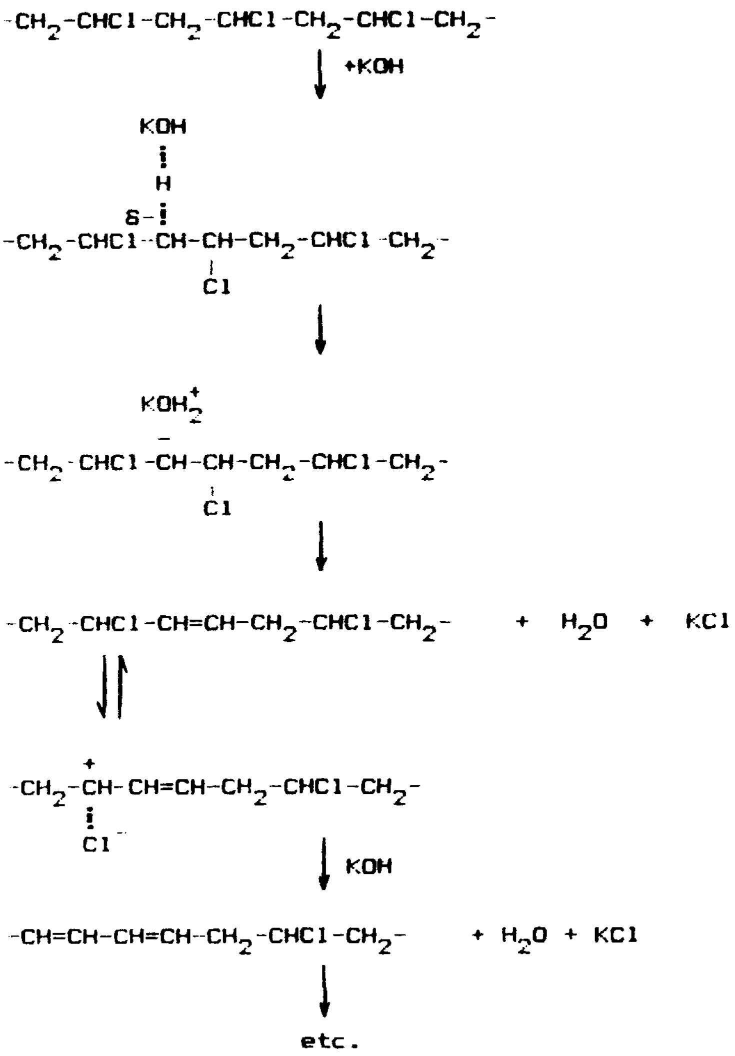


FIGURE 10 Modified reaction scheme of the thermally activated polyene growth by the ion-pair mechanism during chemical dehydrochlorination of poly(vinyl chloride) with KOH in water.

This distribution is verified by several experimental facts, e.g., the formation of benzene during thermal degradation of PVC, which is only possible starting from the trans-cisoid termination structure. The relative content of this structure is 3% and, as is known from the literature,[5] only two benzene rings per 100 double bonds are formed, i.e., both values are of the same order of magnitude.

A more detailed discussion of the connection of polyene formation and chain conformation may be based on the texture model for PVC proposed by Guerrero and Keller.[6,7] According to this model the crystalline phase consists of two types of crystals (see Table II), which differ in their crystalline state, their size, the number of repeats, and their melting range.

If the polyene formation is as closely connected to the conformation of PVC as

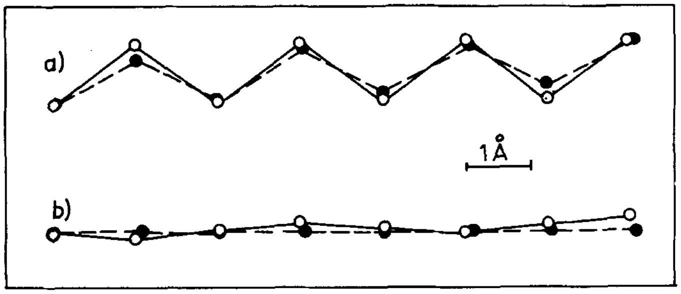
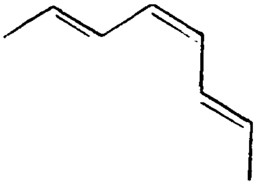
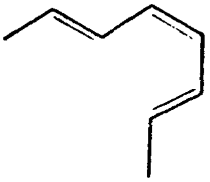


FIGURE 11 Comparison of the geometries of the C—C backbone of the TTTT . . . -conformation of syndiotactic poly(vinyl chloride) sequences and of the trans-polyacetylene.

TABLE I

Possible termination structures of polyenes in poly(vinyl chloride)

PVC-conformation	Termination structure	Content
TTGT (mr)	cis-transoid 	21%
TTG′ (mr)		39%
G′TTG (mm)		14%
G′G′TG′ (mr)	trans-cisoid (I) 	4%
TGTG (mm)		19%
TTGG (rr)	trans-cisoid (II) 	3%
TTTT (rr)	trans-transoid 	(1)

(1) No termination.

we expect, there should also be a close connection to this texture model. To prove this, some examples are shown below.

The first example is according to the interpretation of the temperature-dependence of the sequence length distribution of polyenes formed during thermal degradation above T_g (see Figure 12): the higher the temperature the less probable is the formation of longer polyenes and the difference spectra (Figure 13) clearly demonstrate that with increasing temperature the contents of a special population

TABLE II

Main characteristics of the two crystal populations present in PVC

Characteristic	A-type crystals	B-type crystals
Origin	solutin growth	network juction points
Crystalline habit	lamellar	fringed micelles
Size	≈150 Å	≈40 Å
Number of repeats	> 14 all-trans	≈14 all-trans
Melting range	> 200°C	120–180°C

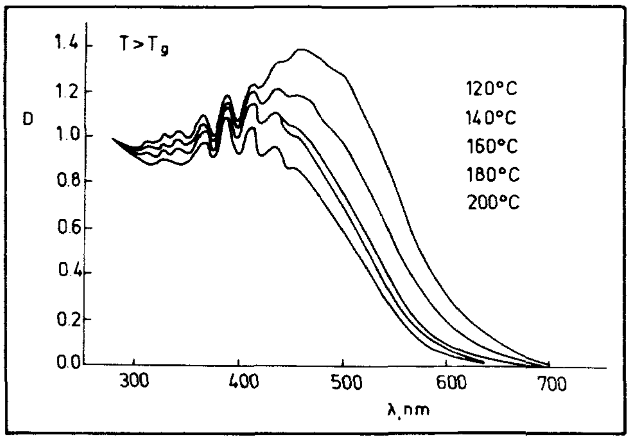


FIGURE 12 Temperature-dependence of sequence length distribution of polyenes formed during thermal degradation above T_g.

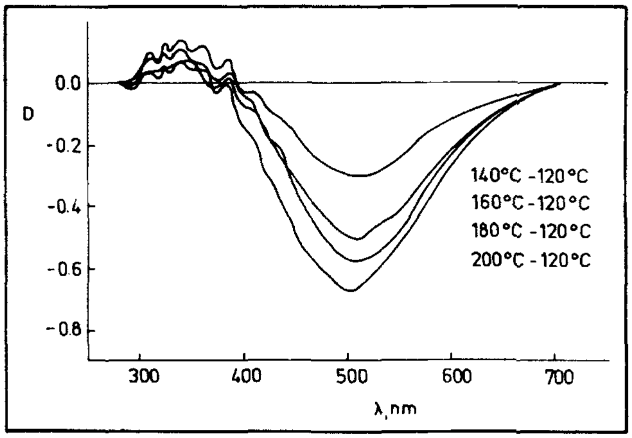


FIGURE 13 Effect of temperature on difference spectra of thermally degraded poly(vinyl chloride).

of polyenes decreases. According to the absorption maximum, at about 500 nm the main sequence length of that population is 14, which means that this population of polyenes is due to the degradation in B-type crystals (compare with Table II).

A second example is the thermal degradation just below the glass-transition temperature (see Figure 14). Besides the formation of short polyenes due to degradation in the amorphous phase, a second population of unusually long polyenes is formed. The absorption maxima at about 550 nm belongs to polyenes of a sequence length of about 25, which means that this population is due to degradation in the high crystalline part of PVC, the A-type crystals.

The formation of A-type crystals, as well as the formation of long polyenes, presume the existence of long syndiotactic sequences deviating from the Bernoullian type of distribution of tactic sequences. The idea that PVC contains a population of long syndiotactic chains has recently been proved by Cuthbertson *et al.*[8] who prepared bulk polymers at very low conversion levels (0, 1–2%). This low conversion material was shown to form long polyene sequences ($i > 15$) during thermal degradation at 190°C. Our results confirm that such a highly crystalline material also exists in a commerical suspension PVC.

This conclusion is further supported by investigations into the formation of polyene during photodegradation. As Figure 15 shows, the polyene sequence length distribution after exposure of PVC films to light of wavelength >310 nm consists of two main populations, representing degradation in the amorphous phase (very short polyenes) and in the highly crystalline phase mainly of the A-type (long polyenes).

This interpretation of the uv/VIS spectra can be proved by investigating the polyene formation in stretched PVC films. According to Guerrero *et al.*[7,9] the larger lamellar (A) crystals align with the lamellar plane parallel to the draw direction, which in this case corresponds to a perpendicular alignment of the syndiotactic chain segments. For this reason, the polyenes formed during photodegradation in the oriented crystals show an unusual dichroism (see Figure 16).

The results clearly indicate a strong correlation between the physical structure of PVC in the solid state and the formation of polyenes during degradation processes. An attempt to interpret the polyene sequence length distribution in terms of the texture of PVC is shown in Figure 17. The actual polyene sequence length distribution mainly depends on the degradation condition. It is interesting to note that during the initial stage of thermal as well as photolytical (at wavelength >310

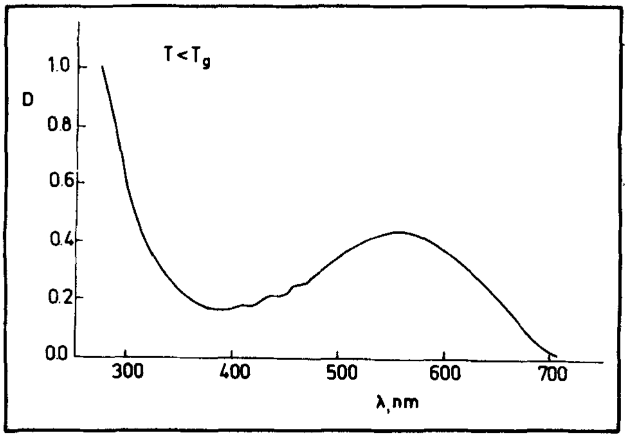


FIGURE 14 UV/VIS-spectra of a thermally degraded sample at temperatures just below T_g.

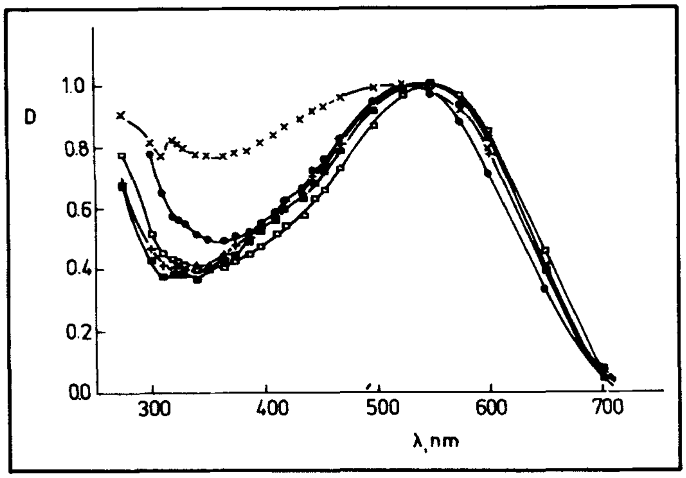


FIGURE 15 UV-VIS-spectra of poly(vinyl chloride) films exposed to light of wavelength greater than 310 nm.

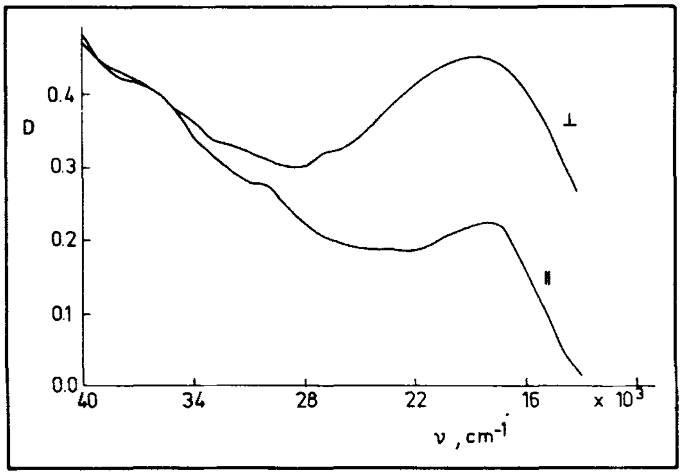


FIGURE 16 UV/VIS-spectra of photodegraded oriented poly(vinyl chloride) films.

nm) degradation of PVC below T_g the dehydrochlorination in the highly syndiotactic crystalline structures seems to be favored. When discussing the long-term stability of PVC products, this fact should be taken into consideration in addition to the initiation at defect sites of the chemical structure of PVC, which is usually considered.

Furthermore, the sequence length distribution of polyenes formed during dehydrochlorination of PVC should be determined by the thermodynamical equilibrium of the PVC chain conformation. To support this assumption we compare the temperature-dependence of the average sequence length of polyenes and the relaxation spectrum of PVC (see Figure 18). The points in Figure 18 represent the average polyene sequence length evaluated from uv/VIS-spectra using the method of Tüdös and Kelen.[10] In the temperature range of from 0°C to 80°C the polyene

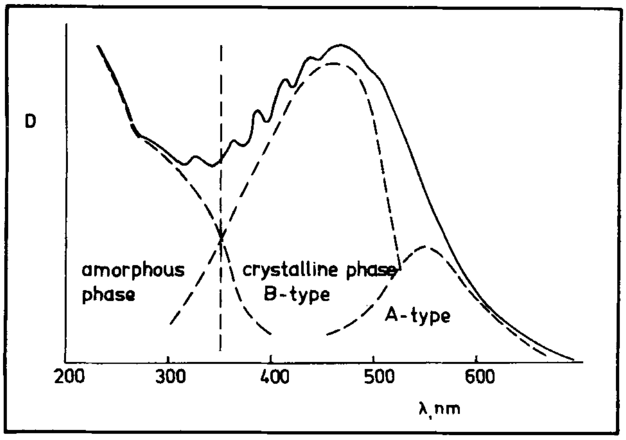


FIGURE 17 Interpretation of degradation processes in terms of the physical structure of poly(vinyl chloride).

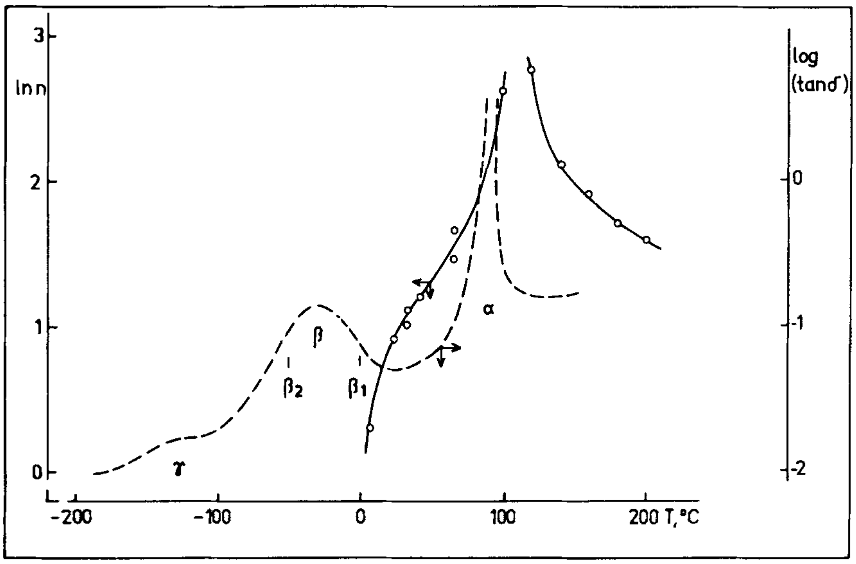


FIGURE 18 Temperature-dependence of the average polyene sequence length compared with a mechanical relaxation spectrum of poly(vinyl chloride).

formation is initiated photolytically, whereas the experimental points above 100°C are obtained from investigations on PVC thermal degradation.

We do not have our own results below 0°C, but as is known from the literature,[11] during irradiation of PVC at -196°C in a vacuum only alkyl radicals are observed by ESR spectroscopy, i.e., the molecular mobility of the PVC chains is restricted to such an extent that even the small atomic rearrangements necessary during transformation from a trans-conformation of the PVC chain to the trans-transoid polyene structure, cannot occur.

However, upon heating of the sample, at about -100°C the alkyl radicals begin to transform to polyenyl radicals, due to the β_2-transition, i.e., the increase in chain mobility in the amorphous part of the polymer. Because of the negligible amount of syndiotactic trans-segments in the amorphous phase of PVC, the average polyene sequence length below 0°C is close to one and the longest polyenes formed are trienes.

Increasing the temperature above the β_1-transition temperature (about 0°C), polyene formation is also possible in the crystalline part of the polymer. This explains the remarkable increase of the average polyene sequence length observed at about 0°C. Above 0°C the average polyene sequence length increases steadily. The corresponding activation energy could be evaluated to (13 ± 3) kJ/mol.

Around the glass-transition temperature of PVC (at about 80°C) a remarkable increase of the average polyene sequence length is seen again. This is due to an increase in crystallinity above the glass-transition temperature, as was observed by Koenig and Antoon[12] while investigating the temperature-dependence of the infrared spectra of PVC. In their paper, Koenig and Antoon also showed that the crystals begin to melt at about 120°C and the conformational heterogenity increases. Subsequently, above 120°C the average polyene sequence length decreases with increasing temperature up to the highest temperature investigated (200°C). For this temperature-dependence an activation energy of (-15.0 ± 0.3) kJ/mol is determined.

Thus, the strong dependence of the sequence length distribution of polyenes formed during dehydrochlorination of PVC on the mobility and the conformation equilibrium of the polymer chains is clearly demonstrated. At least two conclusions may be drawn: (1) Using this conformation concept, it is possible to interpret qualitatively the temperature-dependence of the average polyene sequence length in the wide temperature range of from −196°C to 200°C.

(2) The average polyene sequence length and subsequently the kinetic chain length of the propagation reaction of the polyene growth are determined not by kinetic reasons, e.g., the ratio of the rate constants of propagation and termination, but by the thermodynamical equilibrium of the PVC chain conformation. That is why any attempt in the literature to deduce the sequence length distribution of polyenes formed during dehydrochlorination of PVC by means of a kinetical model failed.

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