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Assignment of UV-Absorption Maxima of Degraded PVC

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Summary

UV-spectra of degraded PVC are put together in a complicated but surveyable way by superposition and deletion of the a-, b-, c-, and d-absorptions of individual polyenes. The existing conception according to which all maxima are based on the most intensive longest-wave d-absorption of a definite polyene sequence could not be confirmed. It has been established that all spectra are showing clearly two additional maxima resulting from a superposition of other polyene absorptions. Thus, counting all maxima for d-absorptions, in the literature a wrong assignment of the UV-maxima to the individual polyenes is reported.

Furtheron, it is shown that the frequency distribution of the polyene sequence length is not influenced by the extent of PVC-degradation, but is mainly depending on the degradation temperature.

Introduction

UV-spectra of degraded PVC have been the subject of several publications in which it has generally been concluded that the coloration of degraded PVC is determined by polyene sequences which vary in length. Because each polyene sequence itself possesses several UV-maxima, the whole spectrum of degraded PVC is put together in a complicated but surveyable way by the addition and obliteration of many, variably strong absorptions. Table 1 summarizes the absorption maxima of distinct dialkyl substituted polyenes in two hydrocarbon solvents, as reported up to n = 5 by Naylor and Whiting(1), n = 6 - 8 by Sondheimer et al.(2), and n = 9 - 13 by Daniels and Rees(3), where n is polyene sequence length. Sondheimer has characterized the maxima as a-, b-, c-, and d-bands, in which the d-band represents the absorption at the longest wavelength.

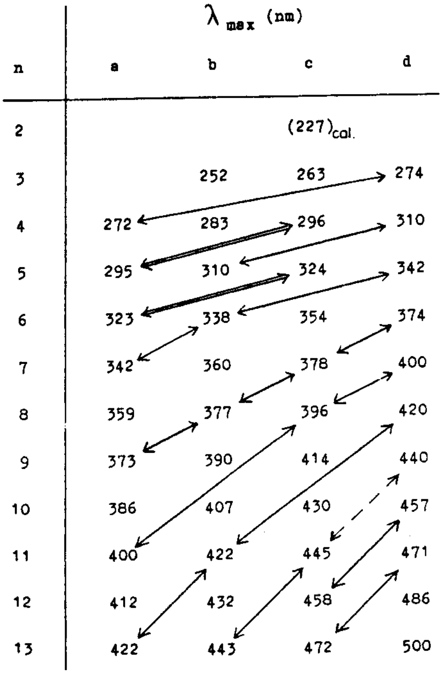
Dienes have only one maximum which must be classified as a c-peak. Trienes and tetraenes show the c-peak as the strongest one. In longer polyenes, however, the d-peak becomes the paramount maximum.

Maxima situated close together are amplified by superposition; in Table 1 they are therefore linked by arrows. Wavelengths of maxima which diverge 6 or more nanometers (nm) from each other are not considererd to contribute to superposition of the absorption maxima.

The most noteworthy feature here is that when the d-maxima are superimposed on the weaker peaks of longer polyenes, there are two combinations of a- with strong c-peaks (4c + 5a and 5c + 6a, see double lined arrows in Table 1) which should result in two strong absorptions in the UV-spectrum of degraded PVC. This and other assignments made in Table 1 could be confirmed by experimental UV-spectroscopy as shown below.

Table 1

UV-absorption maxima of polyenes of the type alkyl-$(CH=CH)_n$-alkyl in hexane and isooctane solutions (according to (1, 2, 3)). Arrows indicate a superposition of peaks.



n	λ_{max} (nm) a	b	c	d
2			$(227)_{cal.}$	
3		252	263	274
4	272	283	296	310
5	295	310	324	342
6	323	338	354	374
7	342	360	378	400
8	359	377	396	420
9	373	390	414	440
10	386	407	430	457
11	400	422	445	471
12	412	432	458	486
13	422	443	472	500

Results and Discussion

The UV-spectrum shown in Fig. 1a is obtained from a PVC-sample partially dehydrochlorinated by means of sodium methylate at room temperature in solution with THF. Taking into account a bathochromic shift of 7 nm caused by changing solvents (THF instead of hexane), the absorption maxima in spectrum a (Fig. 1) agree exactly with the figures corresponding to the d-bands in Table 1.

Up to now in assigning the absorption maxima it was agreed (4, 5, 6) that they are only formed by the most intensive longest-wave d-bands, which also include the weaker absorptions of the longer polyenes. In all spectra, when resolved to some extent, the peaks due to absorption bands 4c + 5a and 5c + 6a are clearly noticeable. They had earlier been accounted for as 4d- and 6d-bands, which resulted in an incorrect assignment of the UV-absorption maxima to the distinct polyenes (c.f. figures in parenthesis in Fig. 1a). Consequently, in the quantitative analysis of UV-spectra, in correctly assigned maxima have caused distorted frequency distributions of the polyene sequence lengths (4).

Degraded PVC always exhibits in its UV-spectrum a strong absorption in the 380 nm region (c.f. Fig. 1, 2 and 3). By Fig. 1a it is evident that this is due to the extended combination 6d + 7c + 8b + 9a absorption maxima rather than to a frequent occurance of polyenes with six conjugated double bonds (hexaenes).

Fig. 1b shows in which way the UV-maxima of the same sample are shifted when

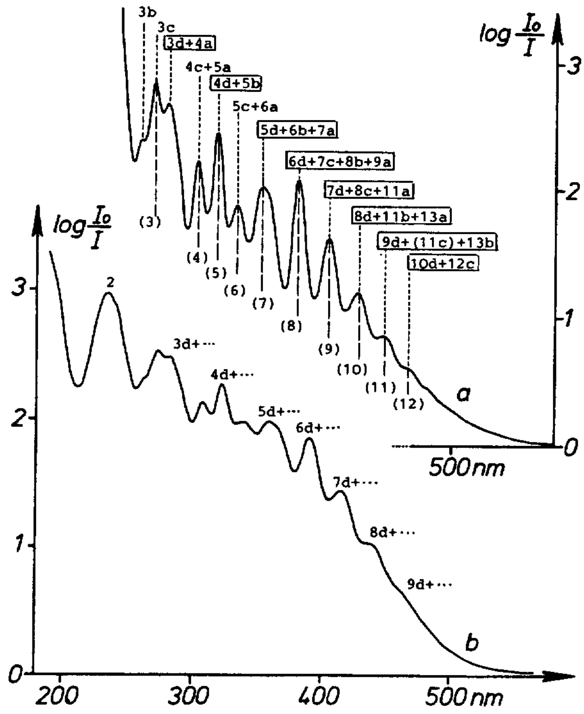


Fig. 1

UV-spectra of degraded PVC (dehydrochlorinated in a THF solution by sodium methylate at room temperature).

a : in solution with THF
b : film (containing THF residues)
☐ : assignments of the d-maxima
(n): previous assignment

the spectrum is recorded from a thin transparent film produced by evaporation of the THF-solvent in a nitrogen-stream, as opposed to in solution with THF. At 300 nm the peaks are shifted bathochromically by about 5 nm, at longer wavelengths (ca. 400 nm) up to about 10 nm.
Fig. 1b furthermore discloses the absorption of the diene portion which, as predicted by Table 1, consists of only one maximum. Absorptions of isolated double bonds are not accessible in an usual UV-spectrum.
In contrast to Fig. 1, the UV-spectra in Fig. 2 have been obtained on pressed transparent PVC-discs degraded to different extents as determined by HCl-evolution at 180°C in a N_2-stream(7). Comparing the spectra in Fig. 1 with those in Fig. 2, it is noticed that in spite of the totally different degradation conditions the characteristic pattern of the peak sequence remains unchanged. From this it can be concluded that in any UV-spectrum of degraded PVC, it is possible to attribute the maxima to distinct polyenes according to the scheme given in Fig. 1a (even without exact knowledge of the corresponding wavelength).
The comparison between Fig. 1 and Fig. 2 also shows the frequency distribu-

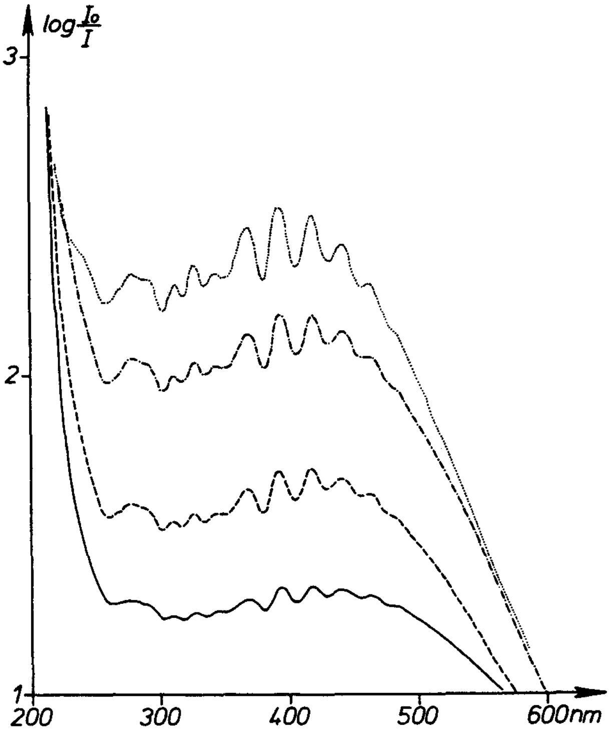


Fig. 2

UV-spectra of degraded PVC. Pressed transparent discs were dehydrochlorinated at 180°C in N_2-stream to the following extent of HCl-evolution:

——— 0.10 %
----- 0.15 %
-·-·- 0.30 %
····· 0.40 %

tion is not influenced by the extent of the HCl-splitt-off, as the four spectra in Fig. 2 demonstrate. With increasing degradation the concentrations of all polyene sequences equally increase, but the average polyene sequence length does not increase. Thus, new unsaturated sites seem always to be created during the PVC-degradation. The creation of new unsaturated sites can be explained by chlorine-radical transfer during the HCl-evolution (8). Such a transfer reaction would become more favoured at higher temperatures, which explains why polyenes formed at 180°C tend to be shorter than those formed at lower temperatures (9). The dependence of polyene sequence length on degradation temperature is convincingly confirmed by the UV-spectra shown in Fig. 3: With decreasing degradation temperature the maximum of the UV-absorption is progressively shifted to the long wavelength absorption region which corresponds to highly conjugated long polyenes. In this case the spectra are taken from PVC-samples which have all been degraded to the same extent as determined by HCl-evolution.

Concluding, only the correct attribution of the absorption maxima in the UV-spectra of degraded PVC is a helpful tool to elucidate the degradation process of PVC, revealing the creation of unsaturated sites and permitting an estimation of the polyene sequence length distribution in degraded samples.

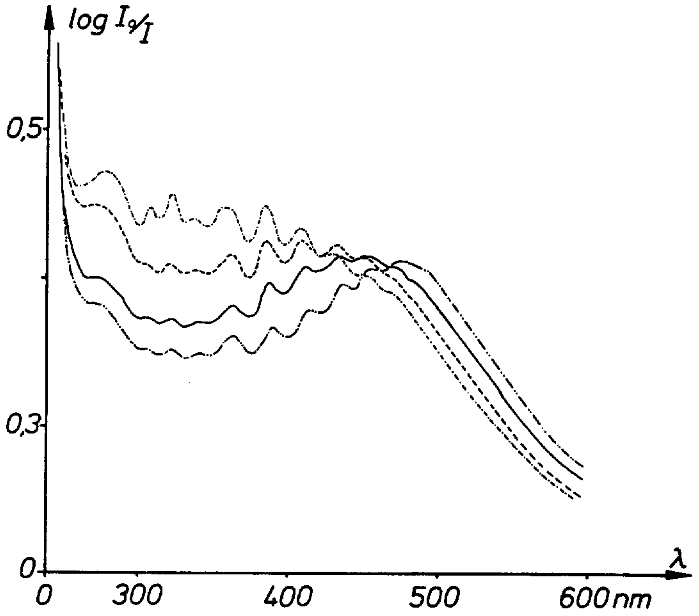


Fig. 3

UV-spectra of degraded PVC samples, dehydrochlorinated in a N_2-stream to 0.08 % HCl-evolution at the following temperatures:
-..-..-.. 110°C, ——— 130°C, ------ 160°C, -.-.-. 180°C.
Spectra are taken from THF-solutions (20 mg degraded PVC dissolved under argon in 3 ml THF).

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