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DEGRADATION OF POLY(VINYL CHLORIDE) FILMS BY X-RAY RADIATION

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Abstract—The X-ray degradation of pure poly(vinyl chloride) films has been investigated by both i.r. and u.v./visible absorption spectroscopy. The transparent films become slightly yellow during irradiation. i.r. Spectra show changes in relative intensities and band position, particularly in the C–Cl stretching region indicating the occurrence of dehydrochlorination and changes in the structure and conformation of the degraded polymer. u.v./Visible spectra of irradiated films show several bands associated with dyenes, carbonyl and many different polyenes and polyenyl radicals. The number of bands increases in the spectra of irradiated samples stored for a long time in air, indicating post-irradiation changes. This effect suggests the formation of polyenyl radicals during irradiation and their subsequent reaction. At the same time, reaction of these radicals with atmospheric oxygen is expected forming C=O groups.

INTRODUCTION

Poly(vinyl chloride) (PVC) has become one of the most important commercial thermoplastic polymer [1] despite its instability to heat and u.v./visible radiations. Consequently, extensive research on several aspects of PVC instability has been carried out [2, 3] in various physical states. In addition, work on the degradation of PVC has been carried out using high energy radiations [4–6], particularly γ-radiation [7–9] and high energy electrons [10,11].

On exposure to u.v. with wavelength above 250 nm [12–17], large amounts of HCl are evolved, together with the formation of conjugated polyene sequences which absorb in the visible range and are responsible for the colour of the irradiated material. Also, the polymer chains undergo both crosslinking and backbone scission while carbonyl and hydroperoxide groups appear in the photo-oxidized polymer.

Under high energy radiations, several reactions can take place in PVC, such as dehydrochlorination, scission of polymer chains and crosslinking, but the former is predominant. The irradiated material shows an increase in the u.v./visible absorption and displays a distinct yellow colouration which increases with exposure time. This yellowing is believed to result from the production of several kinds of free radicals with different half-lives and from conjugated double bond structures (polyenes) containing long sequences of unsaturation, from trapped electrons and other chromophores in PVC, which can remain long after the radiation treatment.

We now report an investigation of the reactions taking place when PVC films are exposed in vacuum to X-ray radiation.

EXPERIMENTAL

Pure powdered PVC used in this study was an unstabilized commercial material from Aldrich Chemical Company. The $\bar{M}_v$ of 98,000, calculated according to a viscometric equation [18], was obtained by using an Ubbelhode viscometer at 25° for tetrahydrofuran (THF) solution.

PVC films were cast from a solution of freshly treated and distilled THF (typically 0.5 g/12 ml of THF) in a dry box under an atmosphere of O_2-free N_2. Traces of solvent were carefully removed by drying at 90° in vacuum (10^{-5} mmHg), for 5 hr. Film thicknesses were *ca* 20 μm.

The PVC films were irradiated with X-rays for various periods at room temperature in vacuum, using a Philips X-ray spectrometer (model PW 1410) equipped with a tungsten tube, operating under 40 kV and 20 mA. The samples were irradiated at a dose rate of 1.15–1.44 MR/hr. The X-ray radiation dose was determined by the thermoluminescence method, using the Harshaw–Nuclear Systems apparatus (model 2000 A) with automatic integrator (model 2000 B).

After irradiation, the u.v./visible spectra of the films were obtained using a Cary 17 spectrophotometer, in the range 200–700 nm. i.r. Spectra were recorded on a Perkin-Elmer, i.r.-180 spectrophotometer, in the range 180–4000 cm^{-1}.

RESULTS AND DISCUSSION

Upon X-ray irradiation, there are several changes in the polymer characteristics, including a yellow to reddish-brown colouration of the film and a change in some mechanical properties of the film (shrinkage and brittleness). It was also observed that the film becomes less soluble in THF. All these changes are enhanced with increase of irradiation time. Due to the low solubility of irradiated PVC in THF, it was not possible to determine the molecular weights for the irradiated samples.

It is known that one of the effects of ionizing radiation on PVC is the liberation of HCl with formation of conjugated double bonds through a radical mechanism. The liberation of HCl and the presence of —(CH=CH)— groups and of conjugated polyenes was confirmed through the changes observed in the i.r. spectrum.

Several Raman and i.r. spectra of PVC have been published [19–24] and the assignment is quite well established both for amorphous and crystalline samples.

On the basis of the vibrational assignments proposed for the PVC chain at different configurations and conformations, a tentative assignment for the i.r. spectrum of X-ray irradiated PVC film has been made.

Due to the liberation of HCl from the polymer, the C–H and C–Cl stretching frequency region and C–H and CH_2 deformation regions must change in the i.r. spectrum.

Figure 1 shows the i.r. spectra of unirradiated PVC films and PVC films irradiated for various periods, in the ranges 3200–2600 and 1800–180 cm^{-1}. Each spectrum was obtained from different films irradiated continuously for 1, 3, 6 and 9 hr and compared with the respective i.r. spectra of unirradiated films. The spectrum (A) of unirradiated film corresponds to that after irradiation for 1 hr. The i.r. spectrum (B) of film irradiated for 1 hr shows a little change in the relative intensities of the bands in the C–Cl and C–H stretching and CH_2 deformation regions, as well as the appearance of a weak shoulder at ~1453 cm^{-1}. The i.r. spectrum (C) of 3 hr irradiated film shows a pronounced change in the relative intensities of the above mentioned bands and the appearance of weak shoulders at ~3020, ~980 and 750 cm^{-1}. The i.r. spectrum (D) of 6 hr irradiated sample shows enhancement of the changes observed in spectrum (C) and contains also two weak bands at ~1645 and 1730 cm^{-1}. The spectrum (E) of 9 hr irradiated films shows a pronounced change in the relative intensity and band position compared to unirradiated films.

C–H stretching modes

The assignments of the CH and CH_2 stretching modes are relatively unambiguous for PVC samples [20]. The i.r. spectrum of pure PVC film shows bands at 2819, 2853 2916, 2939 and 2972 cm^{-1} which are assigned, respectively, to a combination band ($1436 + 1379 = 2815\ cm^{-1}$), $\nu_s(CH_2)$ amorphous phase, $\nu_s(CH_2)$ A_1 mode, $\nu_a(CH_2)$ and $\nu(CH)$.

The i.r. spectrum of PVC film irradiated for more than 2 hr shows a shoulder at ~3020 cm^{-1}; its relative intensity grows with irradiation time. The band in this region can be assigned to ν(CH) of =CH— [25], indicating double bond formation. It is also observed that the band at ~2972 cm^{-1} is shifted to lower frequency and its relative intensity increases remarkably with irradiation time. The frequency shift could be due to increase in the double bond conjugation, but the explanation for increase on intensity is not known.

The intensity of the band at 2820 cm^{-1} decreases rapidly and finally disappears; on the other hand, the band at 2853 cm^{-1}, assigned to the extended non-syndiotactic structure, shifts slightly to higher frequency with an increase in intensity.

CH deformation and skeletal modes

The i.r. spectrum of pure PVC polymer contains no bands in the range of 1800–1440 cm^{-1}, while the i.r.

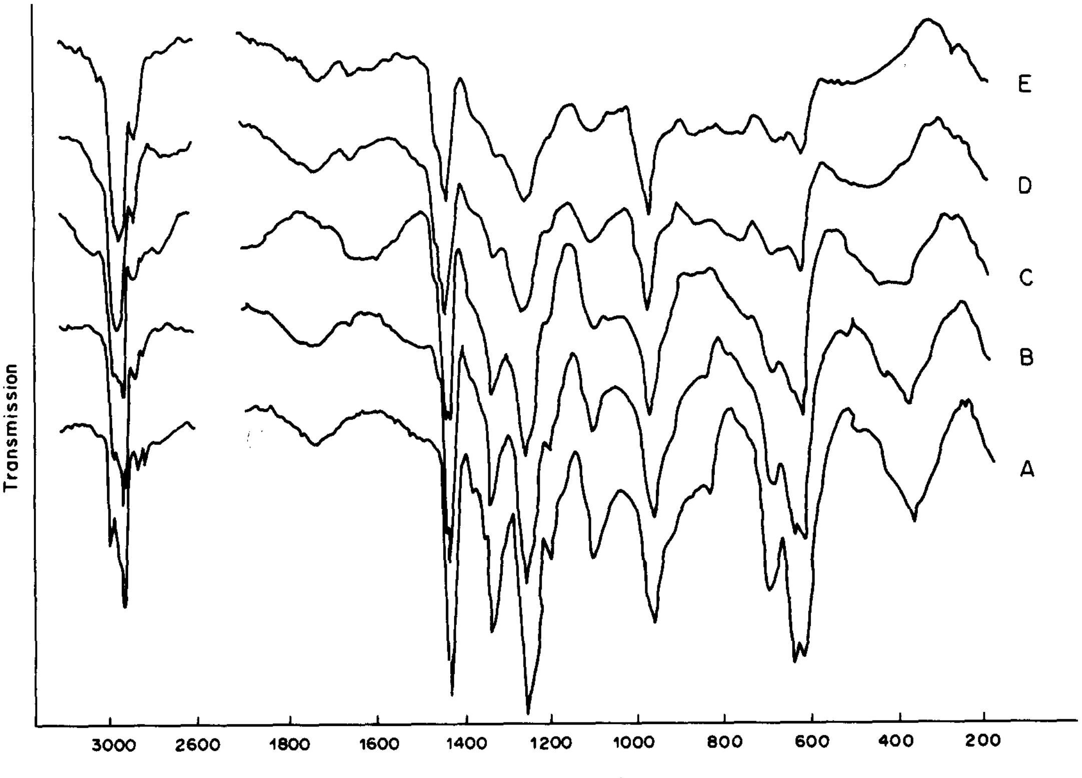

Fig. 1. i.r. Spectra of PVC films: (A) unirradiated; (B) irradiated 1 hr; (C) irradiated 3 hr; (D) irradiated 6 hr; (E) irradiated 9 hr.

spectra of irradiated PVC films show many weak bands and shoulders in this region.

A band at 1730 cm^{-1} can be assigned to ν(C=O), resulting from the attack of atmospheric oxygen on the free radicals formed on irradiation. The weak band near 1650 cm^{-1} is assigned to the ν(C=C) formed by irradiation. Films irradiated for more than 6 hr show, in addition to the band at 1650 cm^{-1}, a weak band near 1600 cm^{-1} or a group of several unresolved bands which can possibly be ascribed to double bond vibrations in polyenes of different lengths. The ν(C=C) stretching frequency varies with the conjugated sequence length and its frequency decreases with increasing chain length. It was not possible to record satisfactory Raman spectra for irradiated samples, because of strong fluorescence. For PVC films, early in the irradiation there is formation of short conjugated double bonds; at later stages, conjugated double bonds of several lengths are formed. It is known [25, 26] that i.r. spectra of compounds containing conjugated carbon–carbon double bonds show at least one strong absorption maximum which shifts toward lower frequency as the length of the conjugated systems is increased.

The bands at 1455 and 1445 cm^{-1} in the irradiated PVC films certainly are related to the in-plane CH deformation vibration, δ_i(CH) of –(CH=CH)– of polyene groups.

The band at 1455 cm^{-1} appears in the i.r. spectrum for 1 hr irradiation and its intensity increases with irradiation time; the band at 1445 cm^{-1} appear clearly only in the 4 hr irradiated film. From these observations it is possible to assign the former band to the δ_i(CH) of *trans*–(CH=CH)– group and the latter to the δ_i(CH) of *cis*–(CH=CH)– group, since the population of *trans* is greater than that of *cis*. The possibility of the 1455 cm^{-1} band being due to δ_i(CH) of short polyene chain and the 1445 cm^{-1} band to the δ_i(CH) of long polyene chains is not completely excluded.

The doublet at 1436 and 1428 cm^{-1} assigned to δ(CH$_2$) amorphous band or extended non-syndiotactic structure and δ(CH$_2$) A$_1$ mode crystalline band which corresponds to the extended syndiotactic structure, do not show any frequency shift with irradiation time, but the relative intensity of the second band decreases with irradiation time.

The D_{1428}/D_{1436} ratio is related to the percentage of syndiotactic segments of the skeleton [27], a value of 1.30 corresponding to 60% of syndiotacticity. With increase of irradiation time, the ratio decreases indicating a decrease of syndiotacticity to less than 40%. Figure 2 shows a curve of D_{1428}/D_{1436} ratio vs irradiation time. The ratio decreases rapidly in the first hour of irradiation and becomes approximately constant after 5 hr of irradiation.

The two bands at 1379 and 1353 cm^{-1} assigned to δ_w(CH$_2$) for pure PVC remain unshifted during irradiation. A band at 1334 cm^{-1} for unirradiated PVC film, assigned to δ(CH) + δ_t(CH$_2$), shifts to lower frequency with increasing irradiation time, shifting to 1310 cm^{-1} for 10 hr irradiation. A band near 1310 cm^{-1} of pure PVC is assigned to amorphous δ_t(CH$_2$).

It is also likely that this band corresponds to the in-plane =CH deformation vibration according to the observation of a strong band in the region of 1310–1290 cm^{-1} in the i.r. spectrum of a series of *trans* disubstituted ethylenes [25].

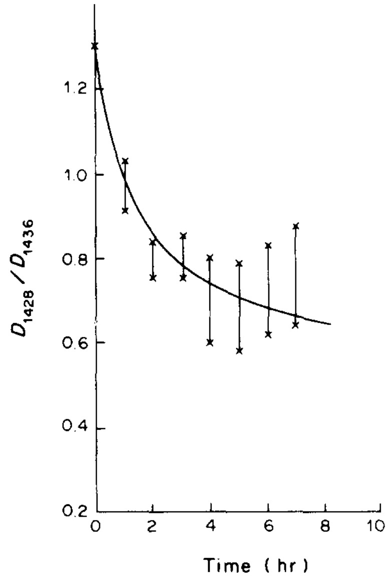

Fig. 2. Intensity ratio of the bands at 1428 and 1436 cm^{-1} vs irradiation time.

The unshifted bands at 1256 and 1241 cm^{-1} could reasonably be assigned to the δ(CH) modes for crystalline and amorphous phase respectively. The relative intensity of the first band decreases with irradiation time.

A band near 1200 cm^{-1}, which remains unshifted with irradiation time, could be assigned to δ_w(CH$_2$) or also to δ(HCCl). Two bands at 1173 and 1078 cm^{-1}, both shifting slightly to lower frequency with irradiation dose, can be assigned to the skeletal modes. Since there is a decrease of C–C bonds with increasing double bond formation, the relative intensity of these bands decreases with irradiation time.

A band at 959 cm^{-1} assigned to crystalline δ_r(CH$_2$) [20] shifts to 969 cm^{-1} for the 10 hr irradiation time spectrum. This band shows a constant increase in frequency with irradiation time and this is a characteristic of the out-of-plane =CH deformation vibration associated with the extended conjugated chain [25]. A shoulder at 975 cm^{-1} is observed in the irradiated spectrum and can also be assigned to the out-of-plane =CH deformation. On the other hand, a band at 970 cm^{-1} of pure PVC is assigned to amorphous δ_r(CH$_2$) [20], so the band at 969 cm^{-1} could be assigned to two vibrational modes, i.e. out-of-plane =CH deformation and amorphous δ_r(CH$_2$). In this spectral region, many vibrations can occur and the reason for the occurrence of two out-of-plane deformation vibrations could arise from different conjugated lengths. The shifting of δ_r(CH$_2$) mode could indicate that PVC with extended syndiotactic structure is attacked by X-ray radiation, leaving the fractions of amorphous PVC which have an irregular and distorted conformation.

A weak band at 833 cm^{-1} which is assigned to crystalline δ_r(CH$_2$), B$_2$ in the unirradiated PVC film shifts to higher frequency with irradiation time up to

850 cm^{-1} for 10 hr irradiation spectrum. This band could correspond to $\delta_r(CH_2)$ of amorphous phase.

There is also the appearance and enhancement with irradiation time of a band at 750 cm^{-1} which could be assigned to the out-of-plane deformation of *cis*-di-substituted ethylenes [25].

C–Cl stretching modes

The ordinary PVC chain can have three different ordered chain structures, the extended and folded conformation for the syndiotactic structure and a helical structure for the isotactic molecule [22].

It is known that the C–Cl stretching frequency ν(CCl) (600–700 cm^{-1}) is very sensitive to the configuration and conformation of PVC chain [21, 22].

Detailed study of a series of secondary alkyl chlorides [28] has shown that the ν(CCl) frequency depends in particular on the substituents which are *trans* to the Cl atom across both adjacent C–C bonds. For example, when both substituents *trans* to the Cl atom are H atoms, the ν(CCl) mode is designated as S_{HH} mode, for a planar zigzag skeletal structure; when one substituent is always C and the other is always H, the mode is designated as S_{HC}; when both substituents *trans* to the Cl atom are the H atom, but when the structure of the carbon skeleton is bent, the mode is designated as S'_{HC}. So it is possible to assign the ν(CCl) modes of non-crystalline bands to rotationally isomeric forms of the chain. The conformation of a chain is determined to a first approximation by the relative configurations of nearest neighbour Cl atoms only. We can designate such adjacent Cl atoms as isotactic pairs or syndiotactic pairs, depending on whether the two Cl atoms are on the same side or on opposite sides of the plane in which the carbon skeleton would assume a standard zigzag form.

Studies of a highly crystalline PVC had shown that bands at 604 and 640 cm^{-1} are associated with the ν(CCl) vibrations of the syndiotactic unit in the planar zigzag chain. The spectra of less crystalline PVC show additional bands in this region, attributable to non-crystalline structures.

The X-ray irradiatd PVC film shows a band at 613 cm^{-1} which can be assigned to an S_{HH} mode and which arises from the syndiotactic pairs and represents the more stable isomeric form.

The band at 693 cm^{-1} assigned to S_{HC} mode must contain contributions from both isotactic and syndiotactic pairs comprising the most stable form of the former and the less stable form of the latter. A band at 638 cm^{-1} is associated with the non-crystalline component and it is possible to assign this to an S'_{HH} mode; its origin can be assigned to the less stable form of the isotactic pairs. A band at 685 cm^{-1} is assigned to a S_{HC} mode of the isotactic pairs. One of the prominent effects of X-ray irradiation is the dehydrochlorination and due to this a decrease of the relative intensity of all bands of the ν(CCl) region is observed and the marked decrease of the intensity of the band at 638 cm^{-1} relative to that of the band at 613 cm^{-1} is clear; a slight shifting of the band at 690 cm^{-1} to low frequency is observed. Figure 3 shows a curve a D_{638}/D_{613} ratio vs irradiation time. The ratio decreases smoothly until 5 hr of irradiation and become approximately constant for longer irradiation. It is also possible to observe a decrease of intensity of the band at 693 cm^{-1} and an increase of intensity of the band at 685 cm^{-1}. These changes could be due to the conformational change of the polymeric chain to the more stable isomeric form.

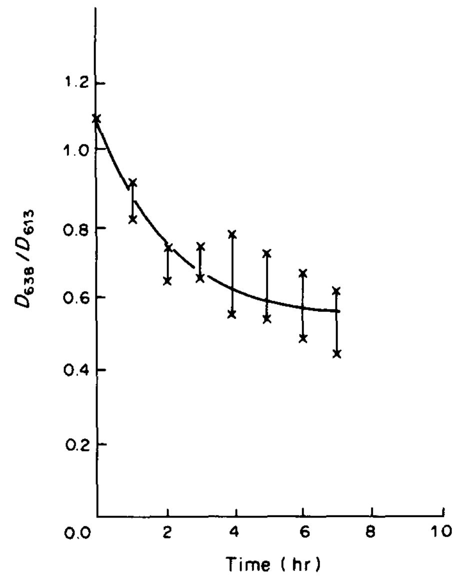

Fig. 3. Intensity ratio of the bands at 638 and 613 cm^{-1} vs irradiation time.

A similar correlation is observed from a study of the spectrum of heated PVC. The effect of heating a typical low crystalline PVC to 180° or of stretching PVC film [21, 29] is to weaken the 638 cm^{-1} band markedly and to cause a shift in the band maximum from 693 to 685 cm^{-1}; the changes were interpreted in terms of conformational changes to the more stable isomeric form of PVC chains.

Despite many investigations on the effects of chain conformation in the vibrational spectra of PVC, the exact correlation among the bands of v(CCl) and the possible conformation that the PVC chain can assume are still uncertain. The assignment considered is based on the study of simple model compounds; this approach may no correspond exactly to the behaviour of the long chain of PVC.

Ultraviolet/visible spectrum

u.v./Visible spectroscopy provides a sensitive method for the characterization of short conjugated polyenes but it becomes increasingly less specific as the sequence length increases.

The u.v./visible spectra show that, with increase of irradiation time, there is enhancement in the absorption at all wavelengths. The unirradiated PVC films absorb very weakly below 250 nm but for films irradiated for 15, 30 and 60 min the spectra show the appearance of bands at 240, 285, 325, 365, 400 and 430 nm (see Fig. 4). These bands can be attributed to polyenes with 3–9 conjugated double bonds [30, 31]. Whichever type of polyene structure is produced when PVC degrades with X-ray irradiation, it is clear that for each molecule formed having n conjugated double bonds there will be several maxima or bands

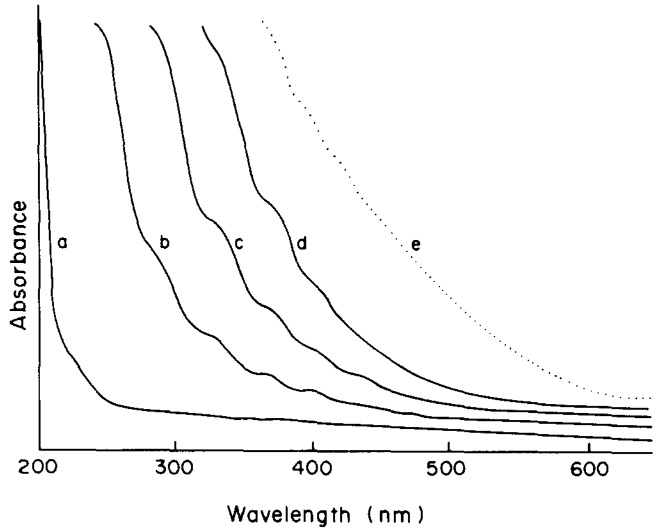

Fig. 4. u.v./Visible spectra of PVC film: (a) unirradiated; (b) irradiated 15 min; (c) irradiated 30 min; (d) irradiated 60 min; (e) irradiated 60 min, after 3 months.

in its absorption spectrum. For 1 hr exposed film, after 3 months of post-irradiation, new bands appear at 385, 412 and 457 nm in addition to the previously existing bands and there is also an increase in intensity of all the bands. Films irradiated for more than 1 hr show strong overlapping of bands, due to the high concentration of polyenes of several conjugated double bonds. Samples irradiated for more than 4 hr did not show clearly resolved bands, but a smooth curve of high intensity, even in the spectrum recorded 3 months after irradiation. With longer periods of irradiation, the absorption at wavelengths greater than 365 nm tends to increase more slowly than does that at 325 nm.

The absorption spectrum of degraded PVC is a superposition of characteristic bands of several polyenes formed during the irradiation, with a very high intensity showing no resolution for film subjected to prolonged irradiation. This is because the red shift of the characteristic bands becomes progressively smaller per unit increase in the sequence length; when a range of lengths is present, as in this case, extensive overlap occurs and the absorption profile is either very blurred or totally lost.

In addition to polyenes, the presence of polyenyl radicals absorbing at wavelengths longer than the correspondent polyenes, can also contribute to the observed band profile. Both the enhancement of the intensity and the appearance of new shoulders with the post-irradiation time can be explained by the reaction of polyenyl radicals formed during the X-ray irradiation. The polyenyl radicals and the polyenes could react with atmospheric oxygen forming C=O groups with a decrease in the conjugated double bonds average length. The C=O groups in the irradiated sample are indicated by the presence of a weak band at 1730 cm^{-1} in the i.r. spectrum of the irradiated sample and by the shoulders at 285 nm in the u.v. spectrum (this band can also be attributed to trienes).

In the absorption spectrum of degraded PVC films, it is not possible to estimate the concentration of several polyenes formed during irradiation, because it is difficult to know the contribution of each polyene to the extinction coefficient at each wavelength.

It is known that there is a superposition of bands due to molecules of different sequence lengths and that polyenes absorbing in the region below 520 nm are associated with a lower number of conjugated double bonds, and those absorbing above 520 nm are those associated with polyenes containing more than 14 conjugated double bonds [30].

It is clear that the concentration of polyenes increases with irradiation time. On the other hand, it is observed that shorter irradiation (<4 hr) favours polyenes having lower number ($n < 6$) of conjugated double bonds and longer periods of irradiation favour polyenes of longer ($n > 6$) conjugated double bonds.

In conclusion, from the vibrational spectra it is clear that the crystalline bands show a change in relative intensity and sometimes shifts, indicating that the X-ray radiation attack preferentially the extended syndiotactic structure region. In the ν(CCl) stretching region, it is evident that the less stable isomeric form is preferentially attacked by X-rays, leaving the more stable isomeric form.

From u.v./visible absorption spectra of degraded PVC, it is clear that a mixture of several polyenes of different lengths and polyenyl radicals are formed with the X-ray irradiation. These structures are believed to be responsible for the development of the yellow to reddish-brown colours of the degraded polymer.

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