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# Investigation of the Photophysical Processes and Photochemical Reactions Involved in PVK Films Irradiated at $\lambda > 300$ nm

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ABSTRACT: This paper is devoted to the investigation of the phototransformation mechanisms of PVK exposed to long-wavelength radiations ($\lambda > 300$ nm) in the absence and in the presence of oxygen. PVK irradiated as thin films was analyzed by fluorescence, UV−vis, and IR spectroscopies. The photoproducts formed were identified by postirradiation treatments including chemical derivatization reactions and HPLC analysis. The cross-linking was evaluated by gel fraction measurements. PVK is known to give an intense excimer fluorescence and no monomer fluorescence. The phototransformations provoked by light absorption are shown to lead to a dramatic decrease of this fluorescence which can be correlated with the modification of the chemical structure of the macromolecules. The decrease of fluorescence is the result of the diminution of the local mobility of the macromolecular chains resulting from cross-linking reactions provoked by the recombination of the several radicalar species. A general mechanism accounting for the phototransformation of PVK in the presence and in the absence of oxygen is proposed.

## Introduction

The photooxidation of polymers can be described by a chain oxidation reaction involving hydrogen abstraction on the polymeric backbone, which leads to the formation of oxidized groups, chain scissions, and cross-links. In the case of polyolefins and nonaromatic polymers, it is admitted that the reaction is initiated by radical species resulting from the absorption of incident light by chromophoric defects and impurities,[1,2] formed along with the processing of the polymers and resulting from the thermal history of the polymeric materials. These modifications generally result in a loss of the initial physical and mechanical properties of the material. On the contrary, most of the aromatic polymers have intrinsic chromophoric units which are able to absorb the near-UV photons of the sunlight.[3] In this case, the oxidation of the polymer can be initiated by radicals that are formed as well by direct absorption of light by the intrinsic chromophores as by light absorption by chromophoric defects. The direct absorption of light by the intrinsic chromophores is also responsible for photophysical processes and direct photochemical reactions.

Among the aromatic polymers, poly(*N*-vinylcarbazole) (PVK) has attracted considerable attention partly due to its photoconductive properties but also to its unusual excimer-forming characteristics. PVK is used extensively as a polymeric photoconductor and to a smaller extent as a holographically optical element. If doped with molecules having a reversible behavior, it enables the recording and the erasing of the holograms, but artifacts resulting from the photodegradation of PVK have been observed to occur during the recording of the hologram.[4]

The photophysics of PVK has been extensively studied. If some studies have been devoted to the photoconductive properties of this polymer under UV exposure,[5,6] most of them concern the excimer fluorescence.[5,7−14] It is reported that no monomer emission can be seen.[7,8,10] The presence of two distinct excimer sites with typical photophysical properties is unique among vinyl aromatic polymers.[13] It has been proposed that the lower energy excimer ($\lambda_{\max} \approx 420$ nm) is formed when two carbazolyl groups have achieved an eclipsed fully overlapping "sandwich-like" conformation.[5,9] This intrachain excimer fluorescence is common to all vinyl aromatic polymers.[12] A 120° rotation about the C−C bond of an isotactic dyad is required to bring two carbazole rings from the ground state to the excimer state where they are totally overlapped.[5,9] On the contrary, the high-energy weakly bound excimer state ($\lambda_{\max} \approx 375$ nm), arising from a partially overlapped structure that involves only one eclipsed aromatic ring from each carbazole group,[5] is specific to PVK. It is thought to involve singlet exciton migration to preformed sites along the polymer chain where the necessary geometrical requirements for excimer formation are satisfied prior to excitation.[5] It means that the polymer conformation appropriate for formation of this state exists prior to the initial excitation step.[5] The tacticity of PVK has been shown to strongly influence the intensity of high-energy excimer emission.[5,11] This second intrachain excimer site is associated with syndiotactic sequences (free radical polymerization) whereas the emission from the true excimer at 420 nm is enhanced in a more isotactic polymer (cationic polymerization).[5,11]

In contrast to the photophysical processes (fluorescence and energy transfer), only little attention has been devoted to the photoaging of PVK. By irradiation of PVK with a high-pressure mercury lamp, Itaya et al.[5] observed the formation of a carbonylated product whose structure was not identified. Pfister et al.[6] speculated, without experimental evidence, on the nature of the numerous photodegradation products of PVK on the basis of known degradation mechanisms of polymers and carbazole chemistry. The reaction expected to occur would be an electron transfer in the excited state of carbazole with oxygen resulting in the formation of conjugated carbazole units and of peroxy radicals. These

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peroxy radicals could lead to further oxidation of the polymer.

As pointed out above, the mechanism of phototransformation of PVK is not elucidated. The aim of this research is to understand the photophysical processes and the photochemical reactions that are likely to occur when PVK is exposed in conditions of accelerated artificial aging ($\lambda > 300$ nm). The purpose is to propose a general mechanism accounting for the phototransformation of PVK in the presence and in the absence of oxygen.

## Experimental Section

PVK powder containing no stabilizers or additives (secondary standard, $M_w$ 1 100 000) and carbazole were obtained from Aldrich. PVK was purified before use by reprecipitation from a dichloromethane solution in methanol. This procedure was repeated three times to remove traces of impurities. Free-standing thin films (10−50 $\mu$m) were obtained by evaporation of a polymer−dichloromethane solution on glass plates at room temperature. The films were then dried in a vacuum at room temperature. The solvent evaporation was carefully controlled by IR analysis.

Photoaging was performed in a SEPAP 14.24 setup based on the conventional SEPAP 12.24 unit[3] but modified in such a way that photodegradation can be performed at 30 °C. This device is equipped with a mercury light source (400 W) allowing irradiation at long wavelengths ($\lambda > 300$ nm).

The cross-linking of PVK was evaluated by gravimetric measurements of the gel fraction. Irradiated films (about 5 mg) were immersed in tetrahydrofuran (5 mL) for 48 h. The solutions were then Büchner filtered. The insoluble fractions were dried in an oven at 100 °C and then weighed.

The fluorescence spectra were obtained using a Perkin-Elmer MPF-3L spectrofluorimeter using a 150 W xenon lamp and the GTI software. The spectra were not corrected for grating efficiency and photomultiplier response. The excitation and emission slits were respectively 6 and 4 nm. IR spectra were recorded on a Nicolet 760 FTIR spectrophotometer (nominal resolution of 4 cm$^{-1}$, 32 scans summation). UV−vis spectra were recorded on a Shimadzu UV-2101PC spectrophotometer equipped with an integrating sphere.

Irradiated films were exposed to reactive $SF_4$ (Fluka) and $NH_3$ (Ucar) gases at room temperature in all-Teflon reactors. Coupling the IR analysis with chemical derivatization reactions allows an in situ identification of the carboxylic acids, esters, aldehydes, and anhydride groups.[15,16]

For vacuum treatments, polymer samples were introduced into Pyrex tubes and sealed under vacuum ($10^{-4}$ Torr) obtained using a mercury diffusion vacuum line.

The macromolecular hydroperoxides formed in the photooxidized samples were titrated using an iodometric method.[17,18]

HPLC analysis of the low molecular weight photoproducts, extracted by immersion of the irradiated films in methanol, were performed on a Merck chromatograph equipped with a photodiode array detector. The column was a Hewlett-Packard reverse-phase C18, 5 $\mu$m (250 × 4 mm). The mobile phase was a gradient acetonitrile (Fisons HPLC solvent)−water (acidified with 2/1000 $H_3PO_4$). The outflow was 1 mL/min.

## Results

**Emission Spectra.** The fluorescence spectrum of PVK shown in Figure 1 was measured under an excitation wavelength at 265 nm. It consists of a band with a maximum around 420 nm that has been formerly assigned to the low-energy excimer.[5] A decrease of this band is observed under irradiation carried out as well in aerated as in deoxygenated media. Further irradiation does not cause the apparition of new fluorescence, contrary to the observation of Itaya et al.,[5c] who observed only little change under vacuum irradiation, but a weak exciplex fluorescence at 515 nm on the spectra of the photooxidized film.

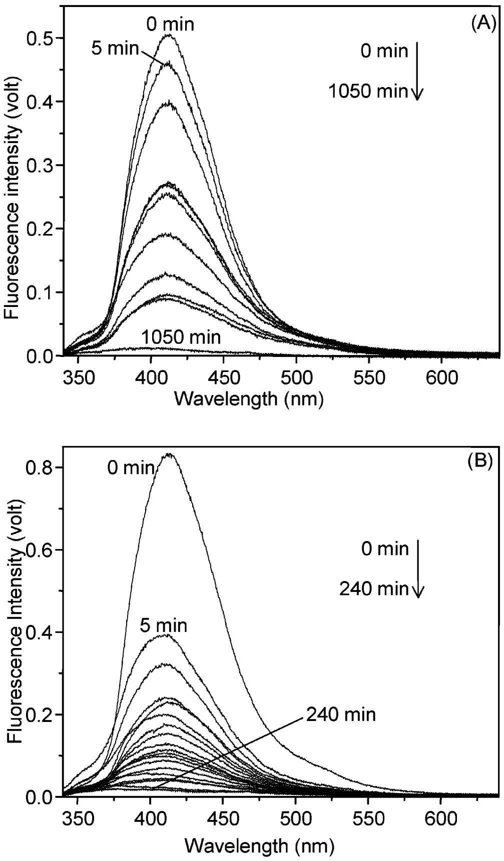


**Figure 1.** (A) Changes in the fluorescence spectra ($\lambda_{exc} = 265$ nm) of a PVK film caused by vacuum photolysis. Irradiation time (min): 0, 5, 30, 92, 150, 210, 330, 450, 530, 810, 1050. (B) Changes in the fluorescence spectra ($\lambda_{exc} = 265$ nm) of a PVK film caused by photooxidation. Irradiation time (min): 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 70, 80, 90, 120, 180, 240.

The results given in Figure 1 show that the total extinction of fluorescence is obtained faster when irradiation is carried out in the presence of oxygen. Around 4 and 18 h are needed when irradiations are carried out respectively in the presence and in the absence of oxygen.

The 265 nm light of the excitation wavelength is totally absorbed within the first micron of the PVK film. To increase the penetration of the excitation light in the film, emission spectra were also recorded by shifting the excitation up to 370 nm. A progressive extinction of fluorescence was also monitored, which indicates that the modification of the structure responsible for the evolution of this photophysical property does not only occur at the surface but also deeper in the bulk (film thickness 25 $\mu$m).

**Evaluation of the Cross-Linking.** PVK films are initially soluble in tetrahydrofuran at room temperature. After irradiation in the presence or in the absence of oxygen, an insoluble part is produced. The amount of insoluble material formed was determined by gravimetric measurements. Results are reported in Figure 2, which shows the increase of gel fraction and compares this evolution with the decrease of the fluorescence intensity. The fluorescence intensity is evaluated as the intensity at the maximum of the emission band at 420 nm.

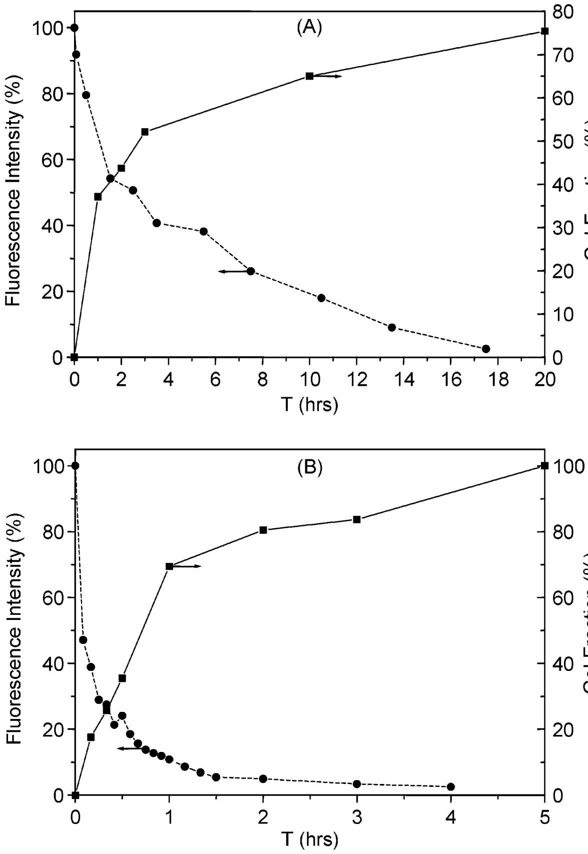


**Figure 2.** Determination of the insoluble fraction (■) and of the fluorescence intensity (●) of PVK films as a function of irradiation time (A) in the absence and (B) in the presence of oxygen.

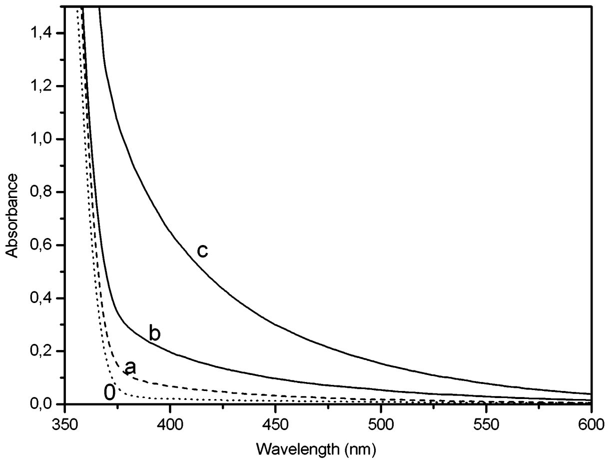


**Figure 3.** UV−vis spectra of PVK films (25 $\mu$m): (0) non-irradiated; (a) after 996 h vacuum photolysis; after (b) 7 h and (c) 50 h photooxidation.

The cross-linking of the polymer and the decrease of the fluorescence occur simultaneously and at low conversion degree of irradiated films. The presence of oxygen during exposure accelerates both these evolutions.

**UV−Vis Analysis.** Figure 3 shows the change in the absorption spectra of PVK films (thickness 25 $\mu$m) caused by irradiation in the absence and in the presence of oxygen. It can be first noted that the light absorption by the carbazolyl group extends up to 370 nm. This makes PVK, as recalled in the Introduction, directly accessible to UV light present in terrestrial solar radiation.

With increasing irradiation time, the development of an unstructured absorption above 370 nm is observed. This absorption is responsible for the photoyellowing of the photooxidized film. On the contrary, when the film is irradiated in a vacuum, the increase in absorption is fairly weak, and no significant discoloration is observed after photolysis.

Figure 4 compares the increase of absorbance at 400 nm with the formation of photooxidation and photolysis products upon irradiation time. Parts B and C of Figure 4 compare this evolution with the decrease of the fluorescence intensity respectively observed in the absence and in the presence of oxygen.

The results plotted in Figures 4 and 2 show that the irradiation time necessary for the formation of UV−vis absorbing species is quite higher than that involved to provoke a cross-linking of the sample and a total disappearance of the fluorescence emission. In particular, Figure 4 shows that no significant evolution in the UV domain can be detected within the first 20 h of photolysis, a period during which extinction of fluorescence and reticulation are achieved.

To visualize the effect of exposure on the absorption bands of the carbazolyl chromophores at 331 and 334 nm, thinner films (10 $\mu$m) cast on KBr plates were irradiated in the absence and in the presence of oxygen. The results obtained show a disappearance of the absorption bands of the carbazolyl chromophores (Figure 5), but only in the case of irradiation in the presence of oxygen. This was accompanied by an increase of absorbance above 370 nm. However, for long exposure duration a decrease of the absorption of the photooxidation products was observed, in agreement with the experimental results of Itaya et al.[5c]

**FTIR Analysis.** Exposure to light of PVK samples (25 $\mu$m) led to dramatic modifications of the infrared spectra of the irradiated samples. These modifications are different in the case of photooxidized or photolyzed samples. The subtraction of the initial spectrum before exposure to the spectra recorded after several exposure times allows the observation of the several maxima that are formed.

Vacuum photolysis of PVK leads to the formation of a band peaking at 3417 cm$^{-1}$ in the range of NH vibrations (Figure 6). In parallel, the decrease of the absorbance of the C−N bond is observed at 1332 and 1224 cm$^{-1}$.

On the contrary, as reported above for the UV−vis analysis, the photooxidation of PVK leads to much more modifications of the IR spectra of irradiated film.

In the 3800−3100 cm$^{-1}$ region (Figure 7A), an increase of an absorption band is observed in photooxidation with several maxima at 3511 cm$^{-1}$ (free alcohols and hydroperoxidic groups[19,20]), 3417 cm$^{-1}$ (as in photolysis), and around 3230 cm$^{-1}$ (associated OH groups of acids[19,20]). The broad band centered around 3230 cm$^{-1}$ becomes preeminent as irradiation proceeds. Such an evolution is classically observed in the photooxidation of aromatic polymers and attributed to the accumulation of carboxylic acid groups.[3]

In the 1900−1550 cm$^{-1}$ region (Figure 7B), photooxidation leads to the formation of maxima or shoulders at 1835, 1770, 1728, 1687, and 1655 cm$^{-1}$. As irradiation proceeds, the maximum at 1728 cm$^{-1}$ shifts progressively to 1715 cm$^{-1}$. The IR analysis of the thin PVK

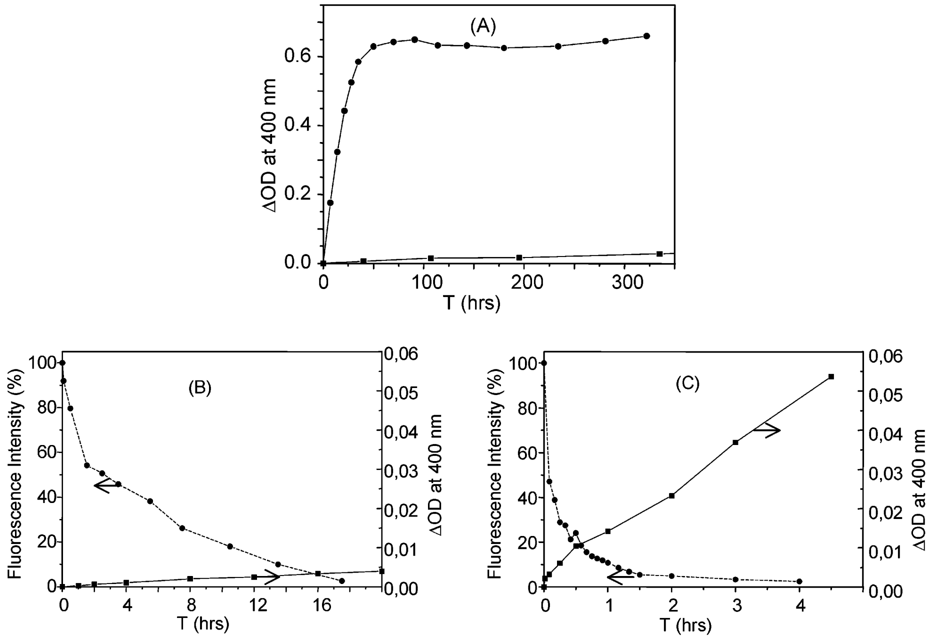


**Figure 4.** (A) Increase of absorbance at 400 nm of PVK films irradiated (●) in the presence and (■) in the absence of oxygen as a function of irradiation time. Increase of absorbance (■) at 400 nm and decrease of the fluorescence intensity (●) as a function of irradiation time of PVK films irradiated **(**B**)** in the absence and **(**C**)** in the presence of oxygen.

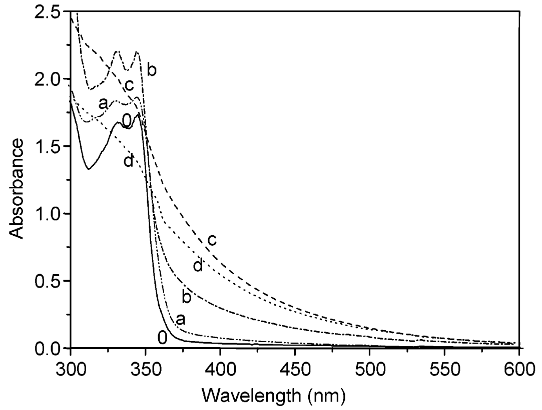


**Figure 5.** Changes in the UV–vis spectra of thin PVK films (10 μm) caused by irradiation: (0) 0 h; (a) after 399 h photolysis; after (b) 9 h, (c) 51 h, and (d) 71 h photooxidation.

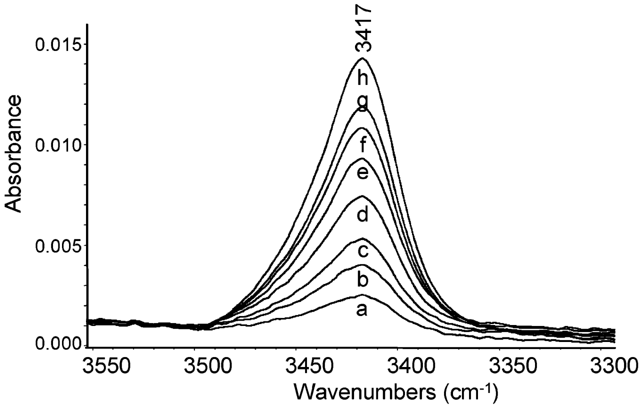


**Figure 6.** Changes in the IR spectra of a PVK film (25 μm) caused by photolysis. Irradiation time (h): (a) 40, (b) 107, (c) 195, (d) 335, (e) 522, (f) 641, (g) 806, (h) 996.

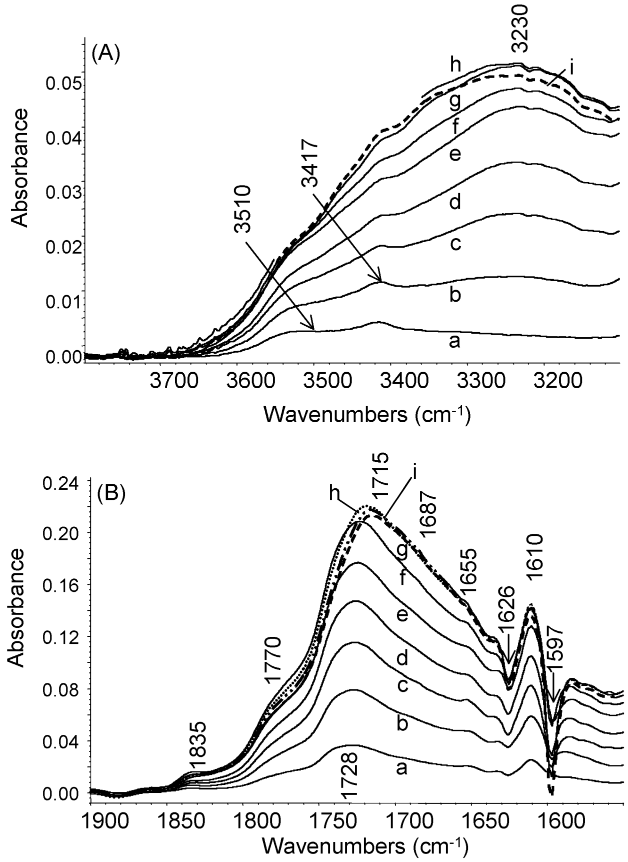


**Figure 7.** Changes in the IR spectra of a PVK film (25 μm) caused by photooxidation. Irradiation time (h): (a) 7, (b) 14, (c) 21, (d) 28, (e) 35, (f) 50, (g) 114, (h) 180, (i) 234. (A) Region 3800–3100 cm$^{-1}$. (B) Region 1900–1550 cm$^{-1}$.

film cast on KBr plates provided a better observation of the maximum at 1835 cm$^{-1}$ and of the shoulder at 1770 cm$^{-1}$.

The development of a thin band at 1610 cm$^{-1}$, located between two ring vibrations of the polymer at 1626 and 1597 cm$^{-1}$, is also observed. The intensity of these two last bands decreases in parallel throughout exposure. As observed with other aromatic polymers,[3] the modi-

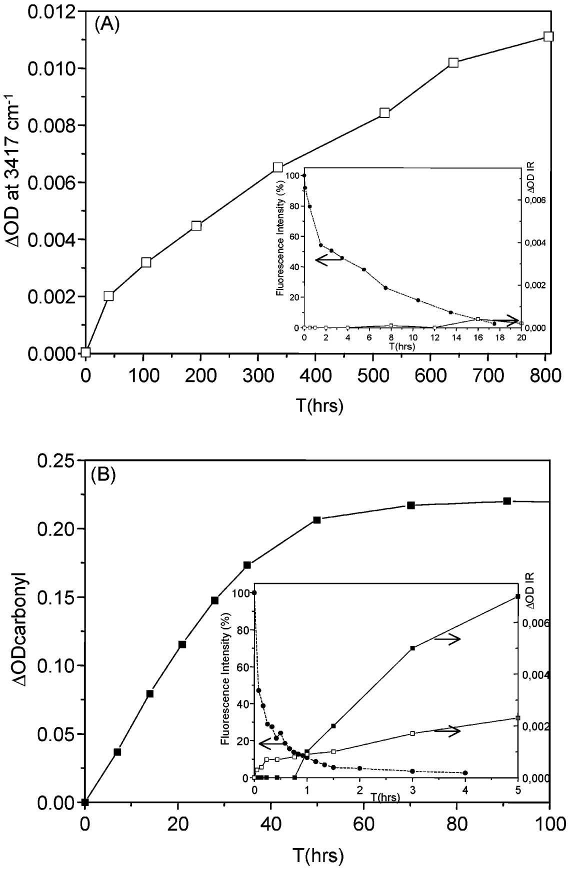


**Figure 8.** (A) Increase of the absorbance at 3417 cm$^{-1}$ as a function of photolysis duration. The inset shows the increase of absorbance at 3417 cm$^{-1}$ (□) and the decrease of the fluorescence intensity (●) of PVK films as a function of photolysis duration. (B) Increase of the absorbance in the carbonyl region as a function of photooxidation duration. The inset shows the increase of absorbance in the carbonyl region (■) and at 3230 cm$^{-1}$ (□) and the decrease of the fluorescence intensity (●) of PVK films as a function of photooxidation duration.

fication in ring substitution may account for such a behavior.

In parallel, an important decrease of the intensity of all the initial absorption bands is observed: for instance, the aromatic $\nu$(C−H) at 3058 and 3022 cm$^{-1}$, the aliphatic $\nu$(C−H) at 2956 and 2932 cm$^{-1}$, the vibration characteristic of the five-membered ring at 1482 cm$^{-1}$ and of the C−N bond at 1332 and 1224 cm$^{-1}$.

The rate of formation of the photoproducts, in the presence or in absence of oxygen, measured by the increase of absorbance in infrared (Figure 8) is observed to follow the same trend as the rate of photoyellowing shown in Figure 4. The two types of modifications involve similar time scales, which are quite higher than the time needed for fluorescence extinction and reticulation. Figure 8 shows in particular that no evolution of IR absorbance can be detected within the first 20 h of photolysis, a period during which both the extinction of fluorescence and the reticulation are achieved.

Irradiation can also produce low molecular weight products, which can be monitored by irradiating the PVK film in a gas cell with KBr windows. The gas phase is then analyzed by FTIR spectroscopy. Only $CO_2$ and water were measured.

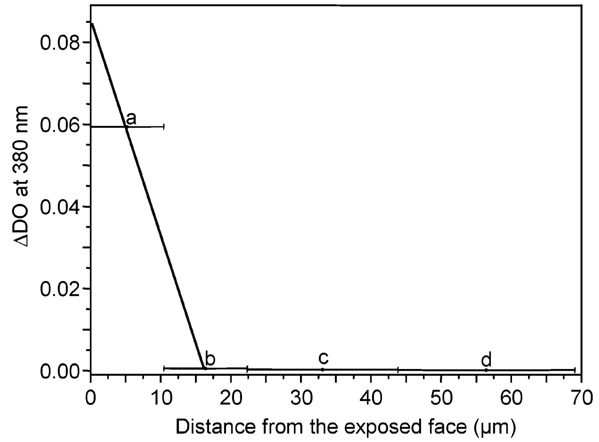


**Figure 9.** Photolysis profile measured by UV analysis of multilayers samples composed of the succession of four films: (a) first film, (b) second film, (c) third film, (d) fourth film.

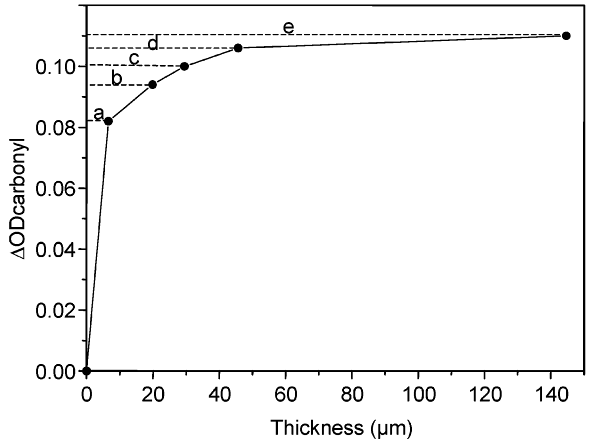


**Figure 10.** Increase of the carbonyl absorption as a function of thickness for PVK films photooxidized 38 h. Thickness of films ($\mu$m): (a) 6.5, (b) 20, (c) 29.5, (d) 45.5, and (e) 144.5.

**Spatial Distribution. Influence of Film Thickness.** A multilayer sample composed of four overlaid thin films (10−25 $\mu$m) of PVK was irradiated for 1200 h in the absence of oxygen. Each film was then analyzed separately, and a profile of evolution was determined by plotting the increase of absorbance at 380 nm for each film as a function of the position of the films in the multilayers assembly (Figure 9).

The obtained results show clearly that the photoproducts are heterogeneously distributed in PVK films: only the first film (15 $\mu$m) is modified. As observed with other aromatic polymers,[3] the limitation of the photoreactions to the first microns can be connected to the attenuation of light passing through the film. The UV−vis spectrum of PVK indicates that light in the near-UV range is totally absorbed within the first 10 $\mu$m (see Figure 5).

The role of oxygen diffusion on the changes observed in the matrix was evaluated in a second experiment. Five films (6.5, 20, 29.5, 45.5, and 144.5 $\mu$m) were photooxidized separately for 38 h (the rear side of the films was not masked during exposure). For each film the increase of absorbance was measured at 1726 cm$^{-1}$. Figure 10 shows the variation of absorbance as a function of the films thickness.

The shapes of the profile plotted in Figures 9 and 10 are analogous. This result indicates that the extent of the photooxidation in the core of the solid sample is not controlled by the diffusion of oxygen and that the only limiting parameter is the penetration of incident light in the film.

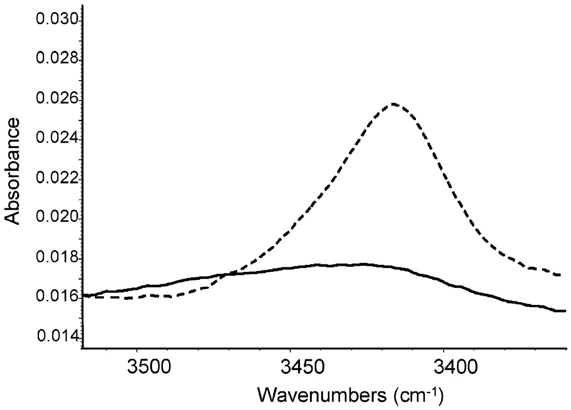


**Figure 11.** Evolution of the IR spectra of a PVK film photolyzed 1291 h (- - -) before and (—) after immersion in methanol for 45 h.

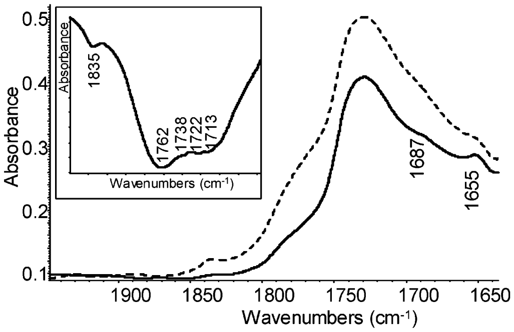


**Figure 12.** Evolution of the IR spectra of a PVK film photooxidized 135 h (- - -) before and (—) after immersion in methanol for 45 h. The inset shows the difference of spectra: after − before immersion.

**Identification of the IR-Absorbing Products.** *Methanol Treatment.* The spectra of photolyzed samples were compared to the IR spectrum of the molecular carbazole. Carbazole and photolyzed PVK both show a band at 3417 $cm^{-1}$ in the range of N−H vibrations.

A film of PVK irradiated for 1291 h in the absence of oxygen was immersed in methanol for 45 h. After methanol immersion, the analysis of the IR spectra shows the disappearance of the band at 3417 $cm^{-1}$ (Figure 11).

The HPLC analysis of the methanolic extraction solution revealed the presence of a low molecular weight product. The retention time and the absorption spectrum of this fraction fitted quite well with molecular carbazole analyzed under the same conditions. This result indicates that irradiation of PVK provokes the scission of the pendant carbazolyl groups which produces by hydrogen abstraction molecular carbazole, trapped in the solid sample. This photoproduct is responsible for the band observed at 3417 $cm^{-1}$ on the IR spectra of photolyzed films.

The presence of molecular carbazole among the extracted oxidation products was also detected. In addition, the immersion in methanol of the photooxidized film (135 h) led to the disappearance of the maximum around 3230 $cm^{-1}$ and to the decrease of the carbonyl absorption between 1850 and 1650 $cm^{-1}$ after a few hours in the solvent (Figure 12). The difference of spectra (before−after immersion) indicates the loss of various types of molecular compounds. On the contrary, the remaining bands at 1687 and 1655 $cm^{-1}$ can be attributed to chain products.

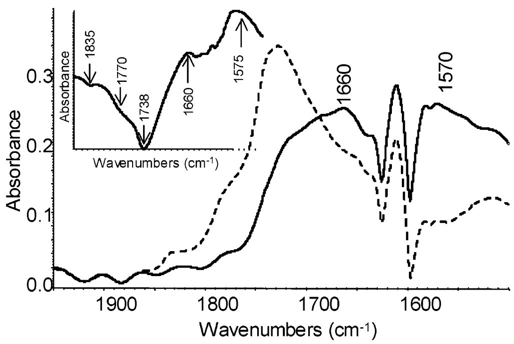


**Figure 13.** Evolution of the IR spectra of a PVK film photooxidized 135 h (- - -) before and (—) after $NH_3$ treatment for 45 h. The inset shows the difference of spectra: after − before treatment.

**Table 1. Hydroperoxides and Mean Carbonyl Groups Concentration as a Function of Irradiation Time**

| irradiation duration (h) | [ROOH] (mmol/kg) | [carbonyl] (mmol/kg) |
|---|---|---|
| 25 | 10 | 215 |
| 50 | 30 | 333 |
| 75 | 48 | 345 |

It can be then concluded that most of the oxidation products, except the photoproduct absorbing at 1687 and 1655 $cm^{-1}$, are low molecular weight products that are soluble in methanol.

*Titration of Hydroperoxides.* Table 1 shows the results of the chemical titration of peroxidic species for photooxidized PVK films (thickness 25 $\mu$m).

The results given in Table 1 show that the hydroperoxides are involved in the photooxidation of PVK but that their concentration remains very low all over the exposure compared to the mean concentration of carbonyl species (calculated from Figure 8B using $\epsilon \approx 350$ L $mol^{-1}$ $cm^{-1}$ and $\rho = 1.184$ g $cm^{-3}$).

*$NH_3$ Treatment.* $NH_3$ treatments were carried out on photooxidized PVK films irradiated for 33 and 135 h. $NH_3$ reactions lead to a decrease in the carbonyl absorption region between 1800 and 1700 $cm^{-1}$ and to the formation of maxima around 1660 and 1570 $cm^{-1}$ (Figure 13). These maxima correspond respectively to amide and carboxylate ions bands obtained after the reaction with $NH_3$ of lactones and esters (observed at 1835, 1770, and 1738 $cm^{-1}$ on the insert) and of carboxylic acids (1713 $cm^{-1}$).

*$SF_4$ Treatment.* The reaction was carried out by submitting photooxidized samples to $SF_4$ gas. Derivatives formed by reaction of $SF_4$ with aliphatic and aromatic carboxylic acids are characterized by a distinct C=O absorption:[15,16] aliphatic derivatives at 1840−1845 $cm^{-1}$ and aromatic and unsaturated derivatives at 1810−1815 $cm^{-1}$. It is recalled that reaction with $SF_4$ is expected to provoke a total disappearance of the OH groups.

PVK films irradiated for 33 and 135 h were treated by $SF_4$ for 168 h. The reaction was not quantitative since only 14% of the absorbance due to hydroxyl groups (3700−3100 $cm^{-1}$) were lost. Reaction with $SF_4$ led to two absorption bands at 1803 and 1846 $cm^{-1}$ coming simultaneously with the decrease of the carbonyl absorption centered around 1718 $cm^{-1}$.

This result indicates that both aromatic and aliphatic carboxylic acids are formed in photooxidized PVK films. Aromatic carboxylic acid structures with IR absorption in the range 1680−1700 $cm^{-1}$ account for part of the

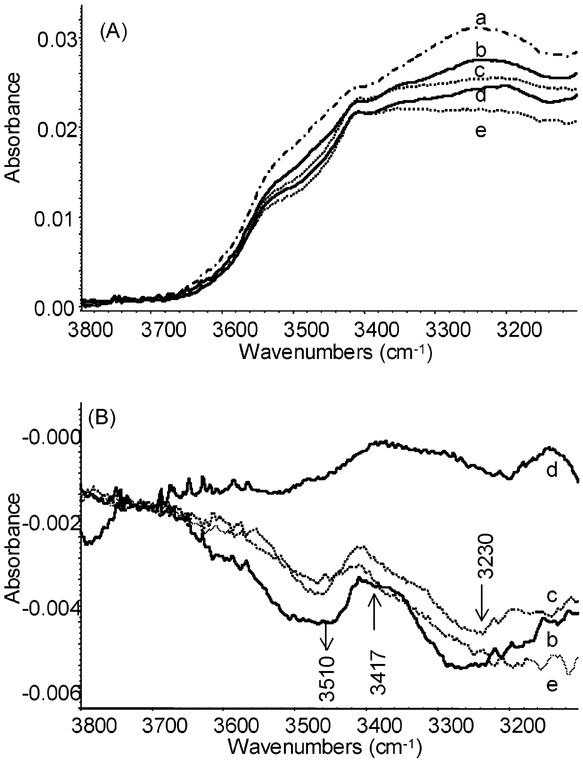


**Figure 14.** (A) Evolution of the IR spectra in the 3800−3100 $cm^{-1}$ region of PVK film (-•-) pre-photooxidized 23 h (a) and submitted to alternate (—) vacuum thermolysis at 100 °C and (• •) photolysis. Duration of vacuum treatment: (b) 50 h thermolysis at 100 °C, (c) 67 h photolysis, (d) 63 h thermolysis at 100 °C, (e) 87 h photolysis. (B) Difference between successive spectra.

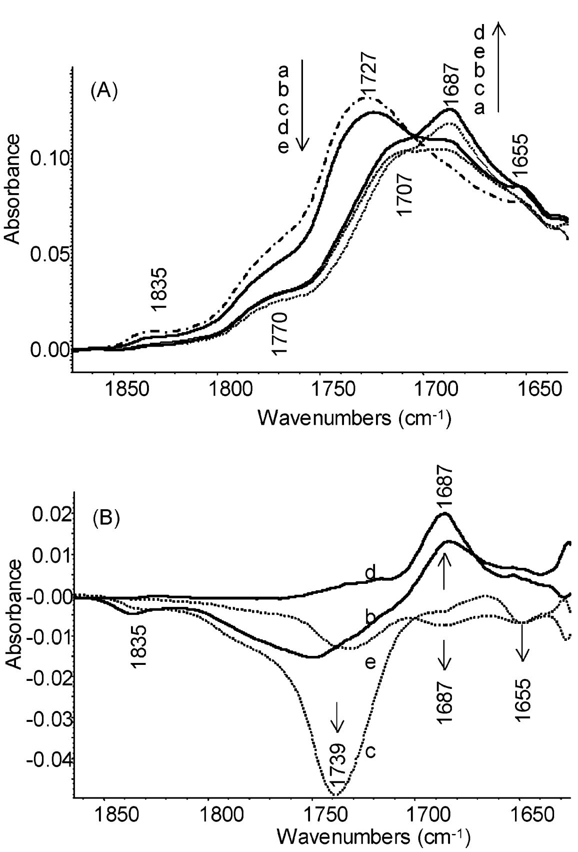


**Figure 15.** (A) Evolution of the IR spectra in the 1900−1600 $cm^{-1}$ region of PVK film (-•-) pre-photooxidized 23 h (a) and submitted to alternate (—) vacuum thermolysis at 100 °C and (• •) photolysis. Duration of vacuum treatment: (b) 50 h thermolysis at 100 °C, (c) 67 h photolysis, (d) 63 h thermolysis at 100 °C, (e) 87 h photolysis. (B) Difference between successive spectra.

carbonyl absorption that gives the fluoride band at 1803 $cm^{-1}$. Aliphatic carboxylic acids with IR absorption in the range 1717−1713 $cm^{-1}$ generate the fluoride band at 1846 $cm^{-1}$.

*Vacuum Treatments of Pre-photooxidized Films.* Thermolysis in a vacuum at 100 °C and vacuum photolysis of PVK films pre-photooxidized can be carried out to check respectively the presence of low molecular products that can be trapped in the matrix and the presence of photounstable chromophoric species. PVK films pre-photooxidized have been submitted to alternate vacuum thermolysis at 100 °C and vacuum photolysis. (Alternate treatments were carried out in order to point out a photothermal equilibrium of yellowing species.)

Both vacuum treatments lead to the decrease of the absorption in the domain of OH and NH vibrations (Figure 14). The disappearance of the absorption observed around 3230 $cm^{-1}$ may be attributed to a loss of low molecular weight carboxylic acids.[19,20] It is accompanied by a decrease of absorbance around 3510 $cm^{-1}$ (Figure 14B) that may be assigned to an homolysis of hydroperoxides. After treatment, the remaining absorption could be attributed to the presence of more stable alcohol groups.

Both vacuum treatments lead also to the decrease of the carbonyl absorption between 1850 and 1600 $cm^{-1}$ (Figure 15). The treatments induce in particular a decrease of the band at 1835 $cm^{-1}$ and of the absorbance in the range 1740−1748 $cm^{-1}$. This latter decrease cannot be attributed to aliphatic ester groups (previously identified by $NH_3$ treatment) as these species are known to be photostable. A potential candidate would be a *N*-cetylcarbazole structure. The IR absorption of this group fits the decrease obersrved in the range 1738−1748 $cm^{-1}$, and this group is known to undergo photo-Fries rearrangement under exposure[21,22] or Claisen-like condensation[3] at high temperature. The formation of this structure will be discussed later.

Differences appeared, however, between photolysis and thermolysis of photooxidized samples.

1. The intensity of the band at 1655 $cm^{-1}$ remains unchanged in thermal treatment but decreases under photolysis. This result suggests that the corresponding product is likely to absorb UV light. The band at 1655 $cm^{-1}$ could be attributed to a quinone−methide structure as previously proposed in the photooxidation of aromatic polymers.[3]

2. Thermal treatment leads to the development of a photounstable band at 1687 $cm^{-1}$ in the range of aromatic ketones, which is not stable under irradiation.

3. In the UV domain (Figure 16), vacuum thermolysis is observed to induce an increase in the UV−vis absorbance of the pre-photooxidized sample. In contrast, vacuum photolysis leads to a decrease of absorbance.

The various products that were identified are reported in Table 2, which summarizes the main results described above.

## Discussion

The results reported above indicate unambiguously that direct excitation of PVK units occurs under irradiation at $\lambda > 300$ nm. Irradiation provokes a rapid decrease of the excimer fluorescence. Shifting the exci-

**Scheme 1. Vacuum Photolysis of PVK**

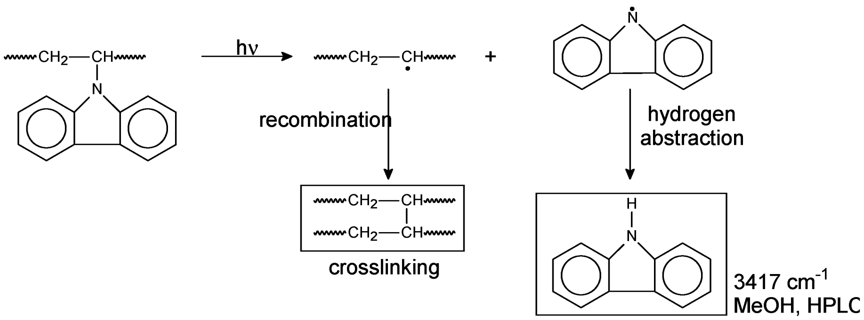


**Table 2. Characteristic Absorptions of the Photoproducts and the Method Which Have Permitted Their Identification**

| photoproduct | | chemical treatment | physical treatment |
|---|---|---|---|
| structure | $\nu$ (cm$^{-1}$) | | |
| quinonic structure | 1655 | | photolysis |
| unsaturated or aromatic carboxylic acid | 1680–1700 | $SF_4$, $NH_3$ | |
| aromatic ketone | 1687 | | photolysis, thermolysis |
| saturated carboxylic acid | 1713–1717 | $SF_4$, $NH_3$ | |
| ester, | 1738–1748 | $NH_3$ | – |
| six-membered lactone, | | $NH_3$ | – |
| *N*-cetylcarbazole | | – | photolysis, thermolysis |
| cyclic anhydride | 1835 and 1770 | $NH_3$, MeOH | photolysis, thermolysis |
| carboxylic acid (O–H) | around 3230 | MeOH | photolysis, thermolysis |
| carbazole (N–H) | 3417 | MeOH, HPLC | photolysis, thermolysis |
| hydroperoxide (ROO–H) | 3510 | iodometric titration | photolysis, thermolysis |

tation wavelength from 265 to 370 nm shows that this decrease occurs as well at the surface ($e < 1$ $\mu$m) as in the core of the sample ($e = 25$ $\mu$m). The decay of fluorescence and a cross-linking of the polymeric matrix occur at the same rate. These phenomena occur even in the absence of oxygen, but oxygen increases their rates. The progressive decrease of fluorescence intensity is not associated with a loss of carbazolyl chromophores: the exposure under vacuum of a thin film cast on KBr revealed no significant modification of the UV spectra. From these results it can be anticipated that the decrease of the excimer fluorescence is related to the cross-linking reactions.

Irradiation of PVK leads also to chain scissions involving the N–C bond. Carbazolyl and macroalkyl radicals are formed. Abstraction of hydrogen by the carbazolyl radical leads to the formation of molecular carbazole that is trapped in the irradiated film (development of a $\nu$(N–H) band at 3417 cm$^{-1}$). This molecular product can be extracted by methanol, and we have identified it by HPLC. The macroalkyl radicals formed simultaneously may recombine together, leading to cross-linking.

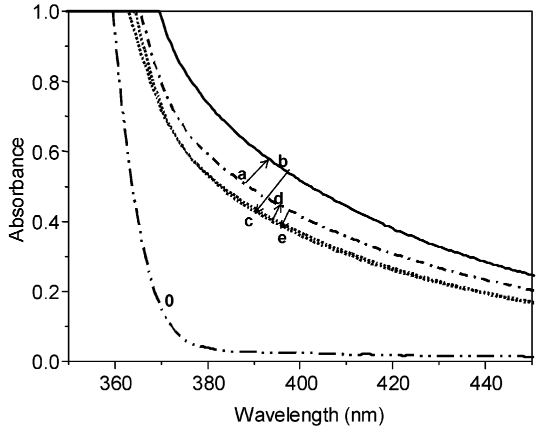


**Figure 16.** Evolution of the UV–vis spectra of a (0) PVK film pre-photooxidized 23 h (a) and submitted to alternate (—) vacuum thermolysis at 100 °C and (• •) photolysis. Duration of vacuum treatment: (b) 50 h thermolysis at 100 °C, (c) 67 h photolysis, (d) 63 h thermolysis at 100 °C, (e) 87 h photolysis.

In the very first steps of exposure no modifications in the IR spectra of photolyzed films are detected whereas a decay of the fluorescence occurs. This is due to the lower sensibility of IR spectroscopy in comparison to emission spectrometry.

Scheme 1 summarizes the main reactions that occur under vacuum exposure.

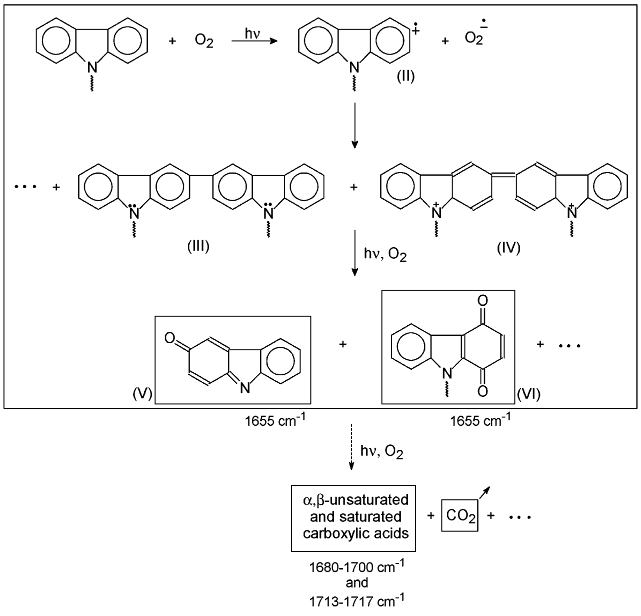
In the presence of oxygen, the rates at which the fluorescence intensity decreases and the cross-linking occurs dramatically increase. The mechanism of photooxidation is quite complex as two possible pathways can account for the formation of the oxidation products that we have identified.

1. Pfister et al.[6] have suggested that electron-transfer reactions could occur in the excited state of the carbazole groups as reported in Scheme 2. The unstable radical cation **II** would lead to the formation of structures **III** and **IV**.

The highly reactive $O_2^-$ can readily form hydroperoxy-type radicals (OOH$^\bullet$) with protons and were supposed to lead to oxidation of the polymer resulting in chain cleavage and oxidation of both the chain and the carbazole ring. It was proposed that the reactions were far too complex to enumerate but that the following functional groups were reasonably expected: $-CH=CH-$, C(O)H, $-CH_2-C(O)-CH_2$ groups; species **V** and **VI** should exhibit absorption to the red of the carbazolyl ring because of extended conjugation.

As shown in Table 2, the products resulting from the photooxidation of PVK and identified by the various treatments are quite numerous. The formation of quinonic structures (1655 cm$^{-1}$) gives evidence for the

**Scheme 2. Photooxidation of the Carbazolyl Moieties**



oxidation of the carbazolyl moieties. Furthermore, the analysis of the IR spectra in the range 1630−1580 cm$^{-1}$ showed the modification in ring substitution.

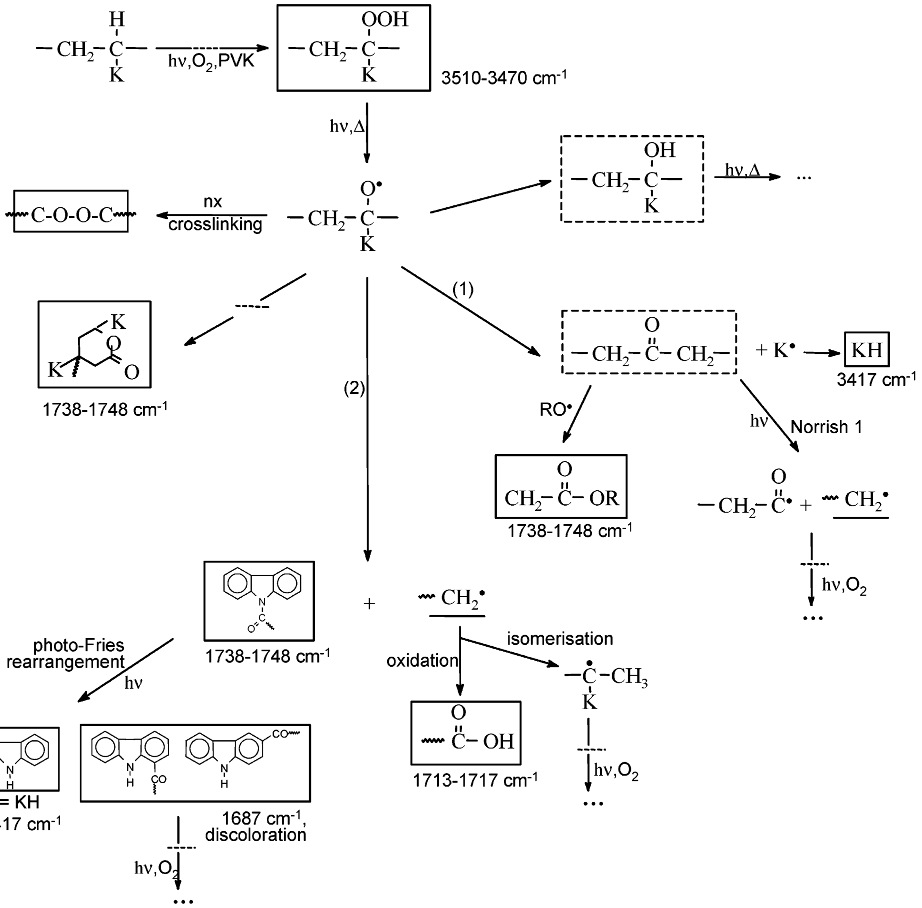
As shown previously in the case of other aromatic polymers,[3] oxidation reactions are not limited to the formation of quinonic structures. The cleavage of the aromatic rings leads also to carboxylic acids and finally to $CO_2$ that can be detected in the gas phase.[3]

It is then possible to complete the proposal of Pfister (frame in Scheme 2) with a mechanism of carbazole moieties oxidation based on our results.

2. Under irradiation in the presence of oxygen, primary macroradicals formed upon direct homolysis of the N−C bond are able to abstract the labile hydrogen atoms of the aliphatic units. These radicals are likely to initiate a chain oxidation by hydrogen abstraction which is generally considered as the first step in the mechanism of photooxidation of polymers[23] (Scheme 3).

The abstraction of a hydrogen atom occurs preferentially at the tertiary carbon of the structure leading to a polycarbazolyl radical; then addition of oxygen forms a peroxy radical. By abstraction of another hydrogen atom, the peroxy radical leads to hydroperoxides (infrared absorption around 3511 cm$^{-1}$). The concentration of hydroperoxides remains fairly low as shown by iodometric titration. The decomposition of the hydroperoxide either by photolysis or by thermolysis gives an alkoxy radical that may react in several ways as reported in Scheme 3: (i) Recombination of two alkoxy radicals leads to the formation of peroxide bridges.[24] Such a process may account for the higher reticulation rate that is observed in the presence of oxygen, compared to the reticulation rate observed in a vacuum. (ii) By abstraction of a hydrogen atom, *N*-alcohol carbazolyl groups are formed. Such groups could participate in the residual absorbance observed around 3500 cm$^{-1}$ after vacuum treatment of photooxidized film. *N*-Alcohol carbazolyl groups are meanwhile supposed to decompose rapidly under exposure (may be after dehydration leading to α,*β*-unsaturated carbazolyl groups). (iii) As proposed for

**Scheme 3. Photooxidation of the Aliphatic Chain**



polystyrene,[23] the reaction of two alkoxy neighboring radicals can lead to the formation of six-membered lactone detected around 1740 $cm^{-1}$. (iv) By $\beta$-scission (1), the alkoxy radical is likely to give a ketone. Former results obtained in our group have shown that this pathway is of minor importance in the photooxidation of vinyl polymers with pendant group (such as polystyrene[23]), which is confirmed by the fact that no absorption was detected around 1720 $cm^{-1}$. Norrish type I reaction of the ketone could be involved. But the identification of ester (around 1740 $cm^{-1}$) would suggest that, once formed, the radical attack of ketone by alkoxy radicals may occur. (v) By $\beta$-scission (2), the alkoxy radical may give a *N*-cetylcarbazole group (detected around 1740 $cm^{-1}$). The $\beta$-scission is accompanied by the formation of an alkyl radical which either can be oxidized into carboxylic acid (1713−1717 $cm^{-1}$) or can isomerize to a tertiary radical.[25] This last radical continues the oxidation process.

As shown by postvacuum treatments, the *N*-cetylcarbazole group may react photochemically by a photo-Fries rearrangement,[21,22] leading to the formation of aromatic ketone (1687 $cm^{-1}$) in ortho or para position plus the corresponding amine which contributes to the development of the N−H band at 3417 $cm^{-1}$. The formation of such structures participates in the modification of ring substitution as observed on the IR spectra (range 1630−1580 $cm^{-1}$). This accounts for the modifications of the spectra of the photooxidized film (decrease of the absorption bands of carbazole and formation of yellowing structures) as shown with *N*-acetylcarbazole. Ortho and para rearrangement products are able to continue the oxidative process under exposure.

No detailed mechanism can be proposed for the formation of anhydride (1835−1770 $cm^{-1}$) since several plausible routes exist.

## Conclusions

The results reported in this paper show that the long wavelengths irradiation ($\lambda$ > 300 nm) of PVK induces the cross-linking of the polymer film without the intervention of oxygen. As a consequence of the decrease of the local mobility that results from cross-linking, a total disappearance of the fluorescence attributed only to the excimer is achieved, after 4 and 18 h exposure respectively in the presence and in the absence of oxygen.

The oxidative degradation involves many routes. The presence of oxygen increases both the rate of excimer fluorescence disappearance and reticulation, probably throughout the formation of peroxide bridges.

The formation of several other oxidation products is evidenced. These products accumulate in the polymer during the first 80−90 h of photooxidation. Their formation is limited to the first 20−30 $\mu$m of the film due to the profile of light absorption in the near-UV range.

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