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Dichromated polyvinylalcohol: key role of chromium(V) in the properties of the photosensitive material

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Abstract

The photochemical behavior of dichromated polyvinylalcohol (DCPVA) films was investigated to elucidate the first step of the reaction taking place in the photosensitive material. The work was completed for comparison by the investigation of DCPVA solutions.

The difference in behavior appears in the ground state and in excited state. Processing a film modifies not only the spectral features of chromium(VI) but also the photochemical behavior. The photoredox process does not occur in basic aqueous DCPVA solution ($pH = 9$) whereas it takes places in films prepared from that solution. The one electron photoreduction of Cr(VI) into Cr(V) is very efficient in both DCPVA films (acidic or basic) with $\Phi = 0.65 \pm 0.05$. The Φ values were calculated from the Cr(V) formation stable enough under the experimental conditions. All the results are in favor of the involvement of a complex between Cr(VI) and OH groups of polyvinylalcohol (PVA). ESR spectroscopy measurements upon irradiation further confirmed the formation and the stability of Cr(V) in PVA matrix. A very nice correlation appeared between Cr(V) behavior and the diffraction efficiency of holograms recorded in DCPVA as reported in the literature.

Keywords: Chromium; Polyvinylalcohol; Photochemistry; Holography

1. Introduction

The photoreactivity of transition complexes has been often used to elaborate or modify polymers in the domain of photography and more recently in holography. Actually the absorption of light by metallic complexes can induce polymerization and/or cross linking of the material. In addition, transition metal complexes exist under different stable valence states and present absorption domain that makes possible the photoreaction upon excitation by visible light. On exposure to appropriate light sources, the sensitizer undergoes a reduction of the metallic center whereas the oxidation causes the formation of a radical on the polymeric matrix.

Among metal doped photosensitive materials used to holographically produce optical elements, dichromated gelatin (DCG) remains one of the best recording materials, although it is one of the oldest photosensitive materials. This is due to its outstanding properties: it provides material with high diffraction efficiency, high resolution, high SNR [1,2], large refractive index modulation capacity, low scattering, and reprocessing. When holograms are used in optical elements, they are usually called holographic optical elements (HOE's). DCG has many characteristics favorable for the elaboration of HOE's. Indeed, one of the indispensable properties is high diffraction efficiency.

However, gelatin is a quite complex macromolecule with a major drawback, the necessary development after exposure that prevents from recording real-time holograms. More recently, better defined polymeric materials such as dichromated polyvinylalcohol (DCPVA) and dichromated polyacrylic acid (DCPAA) have been used to realize various applications in holography and more precisely in real-time holographic recording [3–6]. In such photosensitive materials, only one functional pendent group is present on the polymeric chain, hydroxyl groups in DCPVA and carboxylic groups in DCPAA [7]. The photochemical behavior appeared to be different from that of DCG previously investigated in our laboratory [8]. The overall photochemical behavior of DCPVA was already observed in a previous paper [9] however, some disagreements appeared between the already published results and the results of the additional experiments further performed to elucidate the process taking place during the first stages of irradiation. So the aim of the present work was to investigate the primary photochemical behavior of DCPVA to revisit the global phenomenon and to compare it with that of DCG.

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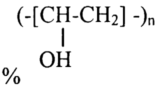
2. Experimental part

2.1. Materials

Ammonium dichromate $(NH_4)_2Cr_2O_7$ was of commercial origin (FLUKA) and used without further purification.

Polyvinylalcohol



$(\text{-}[\underset{\text{OH}}{\underset{|}{\text{CH}}}\text{-CH}_2]\text{ -})_n$

ALDRICH 98% hydrolyzed, $\overline{M}_w$ 13-23000.

All the solutions were prepared in water purified by a Millipore Milli-Q system. The desired pH was achieved by the suitable addition of $HClO_4$ or $(NH_4)OH$ and was controlled to ±0.02 pH unit. The ionic strength was not controlled.

2.2. Apparatus and procedures

2.2.1. Fabrication of dichromated polymer films

DCPVA films have been prepared by the gravity settling method. After the required amount of polyvinylalcohol (PVA) aqueous solution was prepared by dissolving 1.4 g of PVA in 20 ml of preheated water (60 °C), 4 ml of $(NH_4)_2Cr_2O_7$ stock solution (6.25×10^{-2} M) was added (corresponding to a concentration of 2.5×10^{-2} mol l^{-1} in chromium) and stirred to get a uniform mixture. Then a constant volume (1.0 ml) of the above mixture was poured onto a leveled, cleaned glass substrate (size 5 cm × 7.5 cm). It was allowed to dry in a dark chamber under normal laboratory conditions (20 °C and relative humidity = 35–45%) for 24 h, and orange/yellow, clear transparent films with a thickness of 30–40 μm were obtained. The films were peeled from the glass plates only for the ESR spectroscopic measurements.

2.2.2. Irradiation set-up

Monochromatic irradiation of dichromated PVA solutions at 365 nm was performed by using a high-pressure Hg lamp (Osram HBO 200 W) with a Bausch and Lomb grating monochromator. The irradiation beam was parallel, and the reactors were quartz cells of 1 or 0.1 cm path length. DCPVA films were irradiated directly on glass plates. The light intensity was measured by ferrioxalate actinometry ($I_o \approx 1.3 \times 10^{15}$ photons s^{-1} cm^{-2}).

2.2.3. ESR and UV–Visible spectroscopic measurements

The real-time ESR profiles have been obtained by irradiating the dichromated polymer films in a Brucker FR 200D spectrometer at 9.30 GHz with a modulation frequency of 100 kHz. A Xe–Hg Hanovia lamp was employed for irradiation of samples in the ESR cavity. Diphenylpicrylhydrazyl (DPPH, $g = 2.0036$) was used as an internal standard. The evolution of intermediates has been monitored during the course of reaction by the change in the peak-to-peak height of ESR derivative signals. The UV–Visible spectra were recorded on a double-beam Cary 118C spectrophotometer.

3. Results

3.1. Cr(VI)–PVA mixtures

The interaction of chromium(VI) with PVA in both solution and films was investigated by observing the main features of the UV–Visible spectrum of the absorbing species, Cr(VI). With respect to pH (for DCPVA films, pH refereed to the pH of the starting solution), λ_{max} and the molar extinction coefficient ε were measured. Cr(VI) and PVA concentrations were taken as 2.5×10^{-2} mol l^{-1} and 7 wt.%, respectively, in the starting solution. The following method was used to calculate Cr(VI) molar extinction coefficient in the film: a surface S of glass substrate was coated by a known quantity of chromium solution having volume (V), concentration (c) and the absorbance (A), was measured after the film formation (24–48 h of drying). ε value was then calculated from the following equation:

$$\varepsilon(\mathrm{l\,mol^{-1}\,cm^{-1}}) = \frac{AS(\mathrm{cm}^2)}{c(\mathrm{mol\,l^{-1}})\,V(\mathrm{cm}^3)}$$

As previously described [8], Cr(VI) at the concentration used for the work is mainly present in the solution as the dimeric anion, i.e. $Cr_2O_7{}^{2-}$. However, there are no precise information related to Cr(VI) in the film; accordingly total Cr(VI) will be noted Cr(VI) without mentioning the speciation. The UV–Visible spectrum of an aqueous solution of the mixture PVA/Cr(VI) presents a maximum of absorption between 354 and 374 nm according to the pH; it perfectly matches the UV–Visible spectrum of Cr(VI) alone (Fig. 1a). There was no interaction in the ground state between PVA and Cr(VI). This was further confirmed by the ε values as a function of pH (Fig. 1b). The titration profiles of the curves only reflected the protolytic equilibrium between the acidic ($Cr_2O_7{}^{2-}$ or $HCrO_4{}^{-}$) and the basic form ($CrO_4{}^{2-}$) [10]. On the contrary, processing DCPVA films from the corresponding starting solutions induced changes in the spectral features of Cr(VI); λ_{max} is red shifted by 14 nm in acidic medium ($\lambda_{max} = 367$ nm) whereas there was no detectable change in basic medium. As far as ε values are concerned, the changes appeared in acidic medium as well as in basic medium with a non negligible discrepancy among the measured ε values. However, the results clearly evidence the interaction between PVA and Cr(VI) in a DCPVA film. The final chromium species being Cr(III), we also investigated the spectral features of a Cr(III)–PVA mixture in solution: there was no complexation between Cr(III) and PVA contrary to what we observed with gelatin [8] and polyacrylic acid [7].

3.2. UV–Visible study

3.2.1. Photochemical behavior of a DCPVA film

The experiments were performed at pH = 4 and 5.5 the later corresponding to the natural pH of the aqueous solution. Similar phenomena were observed: the spectral evolution

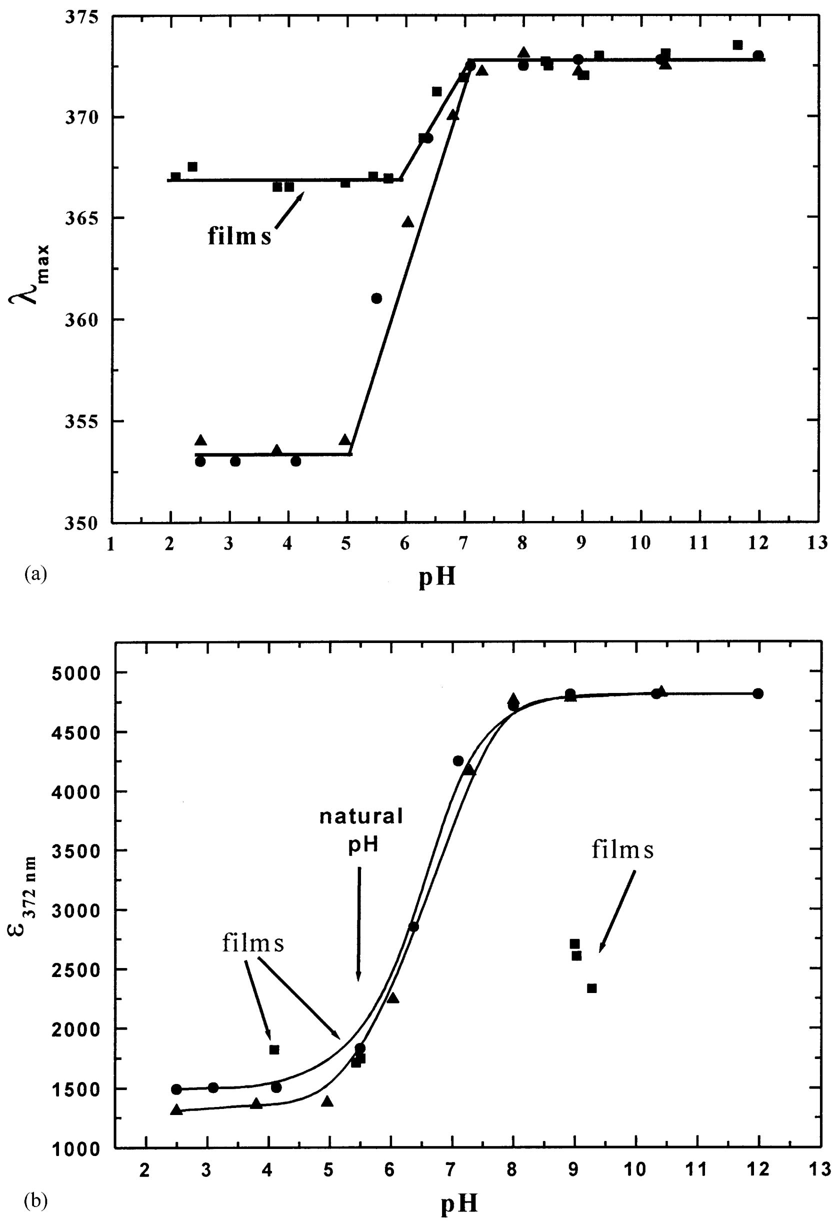


Fig. 1. Evolution as a function of pH of: (a) λ_{max}; (b) ε at 372 nm for (■) DCPVA films, (▲) DCPVA solutions, (●) Cr(VI) solutions ([Cr] = 0.0125 mol l^{-1}; PVA: 7 wt.%).

represented in Fig. 2 reflects the presence for two different domains. A very fast decrease in the early stages of the reaction together with the presence of an isosbestic point at 403 nm and a slow one for longer irradiation, this being similar to what was observed with DCG [8]. By plotting $\Delta\text{Abs} = [(\text{Absorbance})_t - (\text{Absorbance})_0]$ as a function of wavelength, the onset of an absorption was observed with a maximum at $\lambda = 520$ nm (Fig. 3). The initial absorbance of a DCPVA film at 520 nm is negligible under the conditions of concentration, Cr(VI) does not absorb significantly at that wavelength.

The fast increase of the absorbance at 520 nm (Fig. 4) was concomitant with the presence of the isosbestic point and the fast part of the kinetics. It can be attributed to Cr(V) formation through a one electron transfer between Cr(VI) and the organic polymeric matrix as it was already reported for dichromated systems [11]:

$$\text{Cr(VI)} + \text{PVA} \xrightarrow{h\nu} \text{Cr(V)} + \text{PVA}^{+\bullet}\text{(oxidized PVA)}$$

A slow decrease in absorbance at 520 nm was then observed reflecting the disappearance of Cr(V) and the final Cr(III) formation. These results were confirmed by ESR spectroscopy (cf. later).

Accordingly, Cr(V) appeared to be quite stable in DCPVA, and by considering the difference between the rates of Cr(V) formation (very fast) and Cr(III) formation (slow process), we can assume that the second step only takes place after the

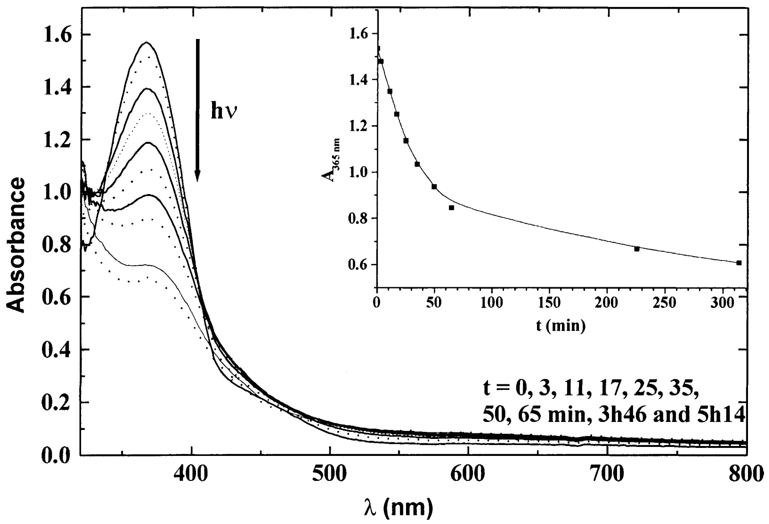


Fig. 2. Spectral evolution of a DCPVA film upon irradiation at 365 nm. Insert: absorbance evolution at 365 nm as a function of irradiation time.

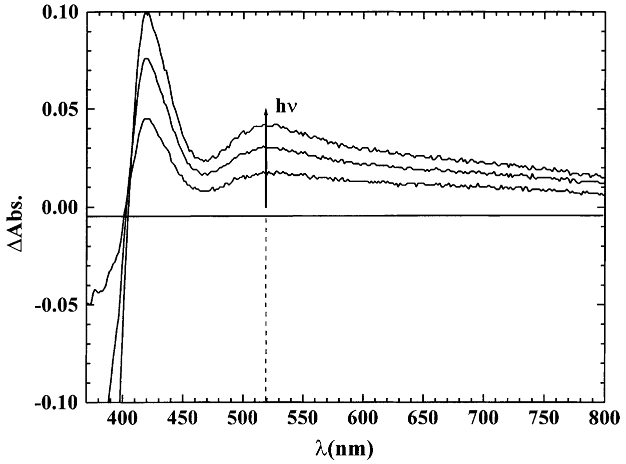


Fig. 3. Difference spectra upon irradiation of a DCPVA film (normal pH = 5.5) between $t = 0$, 3, 11 and 25 min.

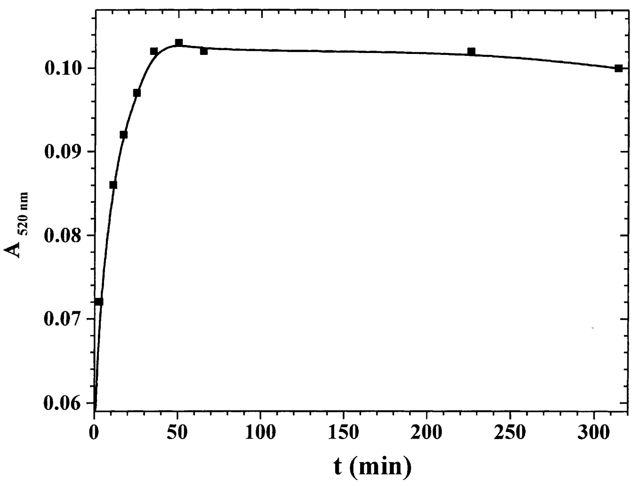


Fig. 4. Evolution of Cr(V) absorbance at 520 nm vs. irradiation time.

complete reduction of Cr(VI) into Cr(V). So the spectrum corresponding to the maximum of absorbance at 520 nm (after about 40 min of irradiation under our experimental conditions) was attributed to pure Cr(V).

From these results, it was possible to have an access to quantitative measurements concerning Cr(V) formation in DCPVA. However, prior the quantum yield calculation, the ε value of Cr(V) at 520 nm has to be determined. Taking into account the previous hypothesis, i.e. the absorbance observed after 40 min of irradiation is only due to Cr(V) absorbance, we were able to calculate it:

$$\varepsilon_{520}^{\mathrm{Cr(V)}} = (67 \pm 7)\,\mathrm{l\,mol^{-1}\,cm^{-1}}$$

The quantum yield of Cr(V) formation was then calculated by the equation:

$$\Phi_{\mathrm{form}}\mathrm{Cr(V)} = \left(\frac{\Delta \mathrm{Abs}}{\Delta t}\right)_{\lambda} \frac{N \times 10^{-3}}{\varepsilon_{\mathrm{Cr(V)}}(I_{\mathrm{a}}/I_{\mathrm{o}})I_{\mathrm{o}}}$$

where $(\Delta\mathrm{Abs}/\Delta t)_{\lambda}$ is the initial slope of the curve giving the absorbance at $\lambda = 520$ nm as a function of irradiation time, $\varepsilon_{\mathrm{Cr(V)}}$ the corresponding values at λ in $\mathrm{l\,mol^{-1}\,cm^{-1}}$, $I_{\mathrm{a}}/I_{\mathrm{o}}$ the fraction of light absorbed by the film, I_{o} the photonic flux at the excitation wavelength, and N the Avogadro number. The photoreduction of Cr(V) by electron transfer from PVA appears to be very efficient with a very high ϕ value:

$$\phi_{\mathrm{form}}(\mathrm{Cr(V)}) = 0.65 \pm 0.05$$

The measurements were performed at different pH's of the starting solution and gave similar values.

The formation of the final Cr(III) characterized by absorption at $\lambda \approx 575$ nm was only effective after days of irradiation or upon irradiation with incident beams of higher intensity [9]. In addition great care has to be taken about PVA purity. Actually it appeared that a few percents of –COOH groups in PVA chemical structure would dramatically change the

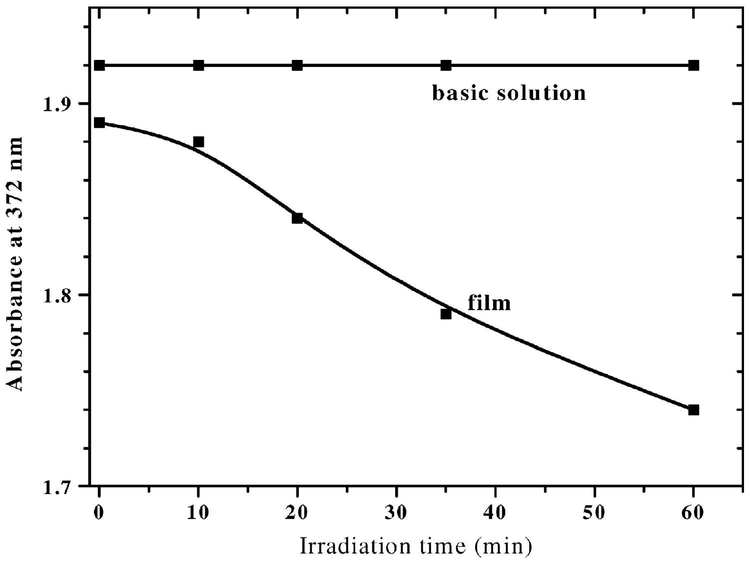


Fig. 5. Photochemical evolution upon irradiation ($\lambda_{irr} = 365$ nm) of a basic DCPVA film and a DCPVA solution ([Cr] $= 4 \times 10^{-4}$ mol l^{-1}) both with pH $= 9$.

photochemical behavior of the chromium species. The work is in progress on mixtures of DCPVA–DCPAA.

3.2.2. *Photochemical behavior of DCPVA solution*

For comparison, the starting solution was also irradiated at 365 nm and it clearly showed that DCPVA solutions behaved on a different way: Cr(VI) reduction was observed in acidic and natural pH solutions (pH $= 4$ and 5.5) whereas in basic solution (pH $= 9$, $Cr_2O_4^{2-}$ species) no photoreduction occurred (Fig. 5).

This last point, when compared to the high reduction quantum yield observed in the films originating from basic solution further confirms that there is an interaction between Cr(VI) and PVA in the film. As we already reported for DCG, there is no possible extrapolation from solution to films in dichromated systems. In addition, great care has to be taken to the humidity during the elaboration of the film: Barikani et al. [12] reported a huge effect of this parameter on the diffraction efficiency of the resulting hologram. The purity of PVA is also an important factor: the presence of COOH groups not only modifies the photochemical behavior as above mentioned, but also the holographic properties [13].

3.3. *ESR spectroscopy*

The formation of Cr(V) was clearly evidenced by ESR spectroscopy upon irradiation with the presence of its narrow signal due to the d^1 electronic structure as already described [14–16].

In DCPVA solution at pH $= 4$, a Cr(V) signal was observed with a hyperfine structure (Fig. 6a) the intensity of which increased with irradiation time, reached a maximum value and then slowly decreased. The signal very quickly decreased when the light was off (Fig. 6b).

On the contrary, the phenomenon observed in a DCPVA film was completely different. Cr(V) signal appeared as a singlet (Fig. 7a) whatever the origin of Cr(V), thermal (in the dark) or photochemical.

In DCPVA films, before irradiation, the presence of Cr(V) from thermal origin was established with a signal at $g = 1.977$ G ($\Delta H = 13$ G), DPPH being used as an internal standard. It corresponds to a negligible quantity of Cr(V), not detectable by UV–Visible spectroscopy. Upon irradiation ($\lambda > 345$ nm), Cr(V) ESR signal first increased and reached a plateau value. A slow decrease was then observed (Fig. 7b). It reflects the fast formation of Cr(V) then its slow transformation into Cr(III). When stopping the irradiation a more complex phenomenon appeared. As it can be observed on Fig. 8 when irradiation was cut off, the signal increased reflecting the fast formation of Cr(V) from thermal origin. The formation of this additional Cr(V) can be attributed to the reaction of Cr(VI) with the radicals formed upon irradiation on the polymeric chain:

$$\mathrm{Cr(VI)} + \mathrm{PVA}^{+\bullet} \rightarrow \mathrm{Cr(V)} + \mathrm{PVA_{ox}}$$

Cr(VI) species being small anions, they can easily diffuse in the polymeric matrix and react with PVA radicals. A similar phenomenon was observed with a DCPVA film prepared from a basic solution (pH $= 9$).

4. Discussion

All the results on DCPVA in solution and film point out the difference of behavior between these two sets of experiments. As far as the starting Cr(VI) is concerned, there is no photoreduction when irradiated in the presence of PVA in basic solution whereas an efficient photoreduction

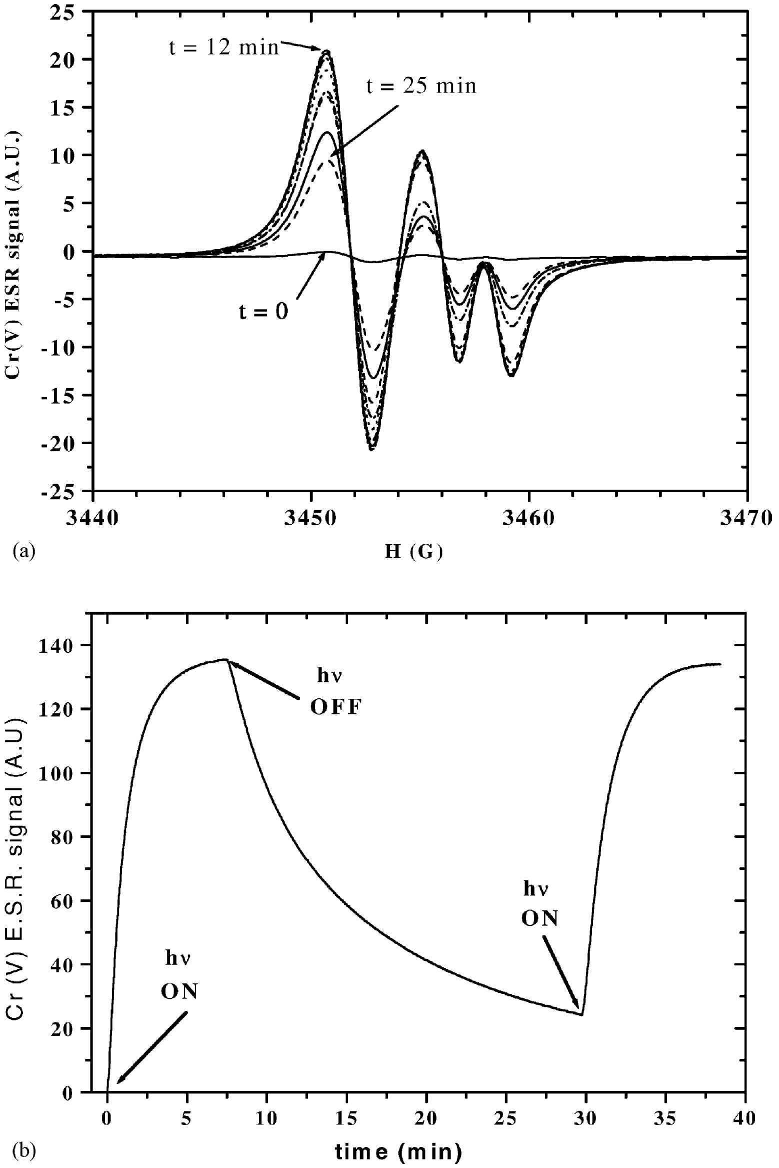


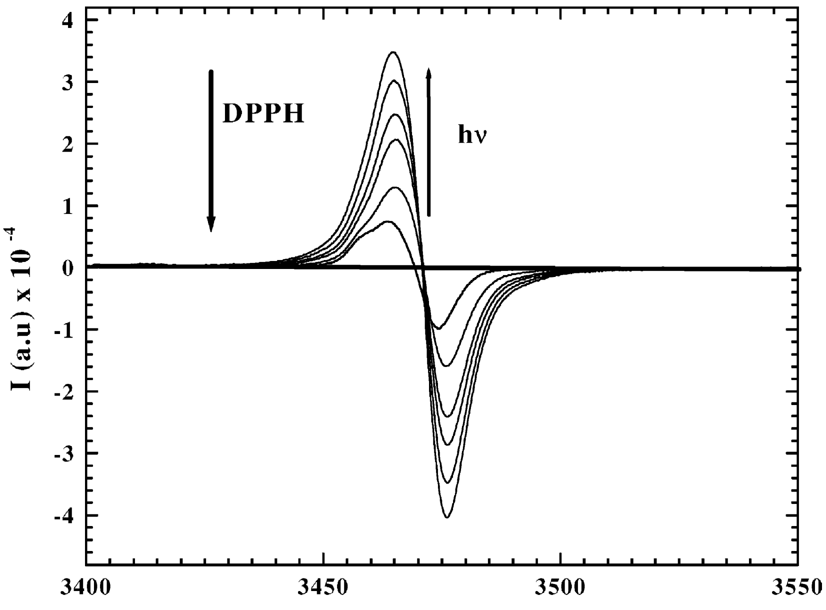
Fig. 6. Cr(V) ESR signal in a DCPVA solution (PVA 3.5 wt.%, [Cr] = 0.0125 mol l^{-1}, pH = 4). (a): Spectral evolution upon irradiation (λ < 345 nm); (b): on-off effect.

process is observed in mildly acidic medium. The observation fits the majority of the results previously reported on similar systems [17,18]. Cr(V) signal formed upon irradiation of a DCPVA solution presents a hyperfine structure; it is unstable which is again comparable to the usual behavior of Cr(V) when the light is cut off.

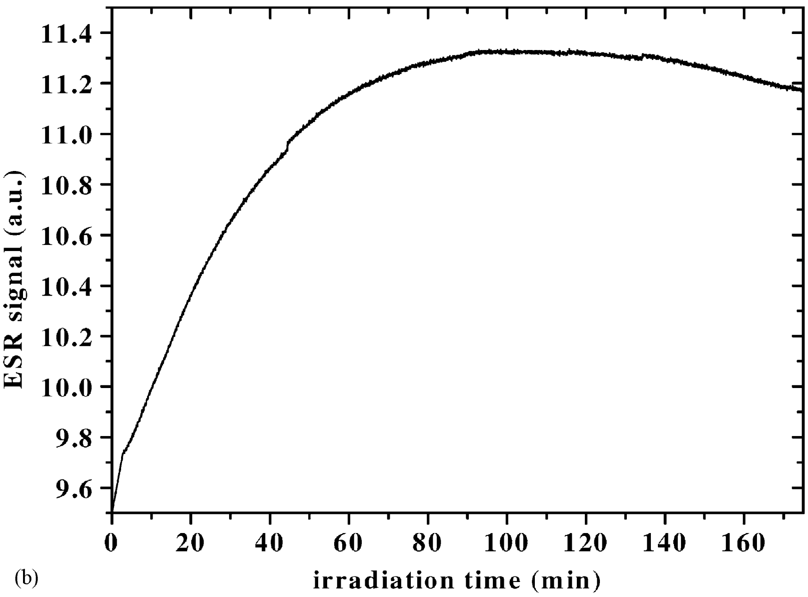
On the contrary in DCPVA films, there is an interaction between Cr(VI) and the hydroxyl groups of PVA as evidenced by the changes in the spectral features of Cr(VI). In addition the photoredox process was also involved when dealing with DCPVA films prepared from basic solution. Such a behavior was already reported in two precise cases: (i) in aqueous system acrylonitrile–Cr(VI) where the polymerization of acrylonitrile photoinitiated by Cr(VI) was observed in basic solution. The results gave evidence for a photocomplexation between acrylonitrile and $CrO_4{}^{2-}$ prior the photoredox process [19], (ii) in DCG. So PVA perfectly mimics gelatin features in terms of pH effect.

Cr(V) ESR signal in a DCPVA film is no longer a structured signal but it appears as a singlet reflecting the interaction between the metallic center and the hydroxyl groups of PVA. The second striking feature of Cr(V) signal is its great stability when the light is off. Among all the results accumulated on Cr(VI)–organic substrate photochemical behavior, only gelatin is reported to complex and stabilize Cr(V). This enlightens on the role of OH pendent groups of PVA chains and of the polypeptidic chain of gelatin.

The reaction and photoreaction between Cr(VI) and alcohols were largely investigated. In the absence of irradiation,



(a)



(b)

Fig. 7. Cr(V) ESR signal in a DCPVA film (PVA 7%, [Cr] = 0.025 mol l^{-1}). (a): Spectral evolution upon irradiation ($\lambda_{irr} > 345$ nm) at $t = 0$, 1, 2, 4, 7 and 10 min; (b) ESR signal evolution upon longer irradiation time.

the most generally admitted mechanism is a two electron reduction of Cr(VI) giving rise to Cr(IV) and a ketone through the intermediate formation of a chromate ester [20]. Upon irradiation a similar process was put forward for years [21] but it is now established that in most cases the first step is a one electron transfer from the organic substrate to Cr(VI), even though, the formation of a chromate ester in which the photoredox process would then take place is still questionable. Such a photoredox process occurring inside a photogenerated complex was assessed for polyacrylic acid in DCPAA [7]. So again we could assume an acido–basic reaction taking place between Cr(VI) species and PVA in the ground state and/or in the excited state.

Further indirect support for the involvement of a complex was given by the unsuccessful attempts to improve the diffraction efficiency of DCPVA holograms by adding electron donors [22] whereas with DCPAA the addition of *N*-*N*-dimethylformamide (DMF) strongly enhances the value of diffraction efficiency [7]: its role was proved to be that of a complexing agent favoring the acido–basic reaction between excited Cr(VI) and PAA.

The second important aspect of the work in DCPVA is related to the similarity of the photochemical primary steps in

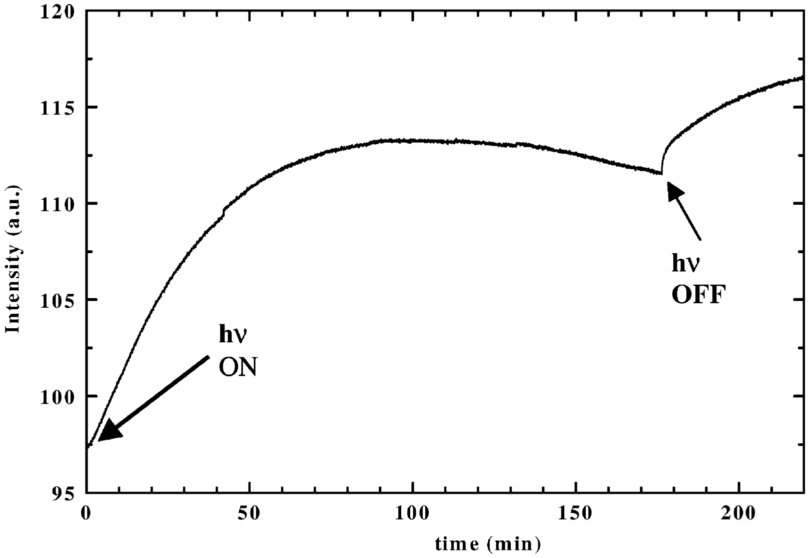


Fig. 8. Cr(V) ESR signal in a DCPVA film: effect of stopping irradiation.

gelatin and in PVA. A very efficient electron transfer occurs with both polymeric materials ($\phi > 0.5$) and a high stabilization of Cr(V) in irradiated films. Keinonen and Grzymala [23] reported the evolution of the diffraction efficiency (that reflects the holographic quality) as a function of exposure time of an acidic DCPVA film: the curve exactly resembles that of Cr(V) formation with a fast increase, a plateau value and additional increase when the writing light was off. When correlating the whole set of results, it appears that Cr(V) is directly responsible of the hologram formation in DCPVA. Some more works are in progress with other dichromated systems in order to check the possibility of generalizing this conclusion.

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