Origin of the Photo-Cross-Linking Process in Dichromated Polyacrylamide under Conventional and Laser Irradiation

Audrey Berger, Lawrence Frezet, and Yaël Israëli*

Laboratoire de Photochimie Moléculaire et Macromoléculaire, Unité Mixte de Recherche Université Blaise Pascal/Centre National de la Recherche Scientifique 6505, 24 avenue des Landais, F- 63177 Aubière, France

Received: April 8, 2009; Revised Manuscript Received: September 4, 2009

This work is devoted to determining the contribution of amide groups in the photoredox and cross-linking process of dichromated polyacrylamide based on the fate of the photoactive species and of the polymer under conventional and laser irradiation. It was shown that, in parallel to the reduction of chromium(VI) into chromium(V), the cross-linking of the matrix occurred through a complexation reaction around chromium(V) and through formation of covalent bonds between macromolecular chains. A comparison with dichromated poly(vinyl alcohol) was also reported to highlight the role of the chemical structure of the polymeric matrix in the mechanism of hologram formation. Moreover, for the first time it was demonstrated by in situ infrared spectroscopy that the physicochemical modifications undergone by the photosensitive materials were similar for the two modes of irradiation.

Introduction

In recent years, holography has attracted great interest due to its potential applications. In particular, it plays an important role in optical data storage with large storage capacities and fast data transfer rates.[1–4] The success of holographic applications depends on the performance of the recording materials, such as dichromated materials, photopolymers, and photoresits.[5] Among them, dichromated gelatin leads to the formation of the highest quality holograms, but it prevents real-time holographic recording. For many years, our group was interested in dichromated polymers, such as dichromated poly(vinyl alcohol), DCPVA, and poly(acrylic acid), DCPAA,[6–11] which are self-developing materials and contain only one of the functional groups present in gelatin. From a physicochemical point of view, our aim was to elucidate the specific role played by each functional group in the hologram formation mechanism. For this purpose, we applied a molecular and macromolecular approach based on the fate of both chromium, the photoactive species, and the polymeric matrix. The combined approach performed in DCPVA, showed that the photoredox process, which involves a one-electron transfer from the polymeric matrix to the metallic cation, takes place in two successive steps. Chromium(VI) was reduced to chromium(V), which was itself slowly reduced to chromium(III).[10] Each step of the reduction was accompanied by the oxidation of OH groups of PVA into ketone groups and the formation of carboxylate functions on the polymeric chains, respectively. From this study, it was established that chromium(V) not only was an indicator of the quality of the holograms, but it was also responsible for the formation of the holograms because of its ability to bridge the polymeric chains to each other.[10]

This combined approach also allowed us to elucidate the role played by the ammonium cations in the hologram quality, that is to say, why ammonium dichromate-doped PVA yielded better holograms than potassium dichromate-doped PVA. It revealed that the enhancement of the hologram quality was assigned to amide groups. These groups result from PVA phototransformation and provide additional chelating sites toward chromium(V).[10]

This present work was devoted to understanding the contribution of amide groups in the photoredox and the cross-linking processes. To this end, we investigated the physicochemical changes of both the photoactive chromium species and the polyacrylamide, PAM, matrix occurring at 365 nm, a wavelength widely used to elucidate the photochemical process in dichromated systems. A combination of analytical techniques, UV−visible, electron paramagnetic resonance, and infrared spectroscopy was used to follow the fate of both the absorbing species and the polymer. The cross-linking process was monitored by insoluble fraction measurements in water. To our knowledge, no photochemical and holographic studies of dichromated polyacrylamide, DCPAM, as a photosensitive material used in holography have been reported in the literature, whereas, acrylamide-base photopolymers have been investigated for holographic data storage.[12–18] The physicochemical changes of DCPAM will be compared to the ones occurring in DCPVA in order to point out the specific role played by the CONH$_2$ and OH groups, respectively.

For a long time, it has been established that in dichromated systems, the primary photochemical process was similar under conventional excitation (exposure at 365 nm) and under laser excitation (488 or 514 nm) but only based on the fate of the chromium species.[19] But one can ask about the polymeric matrix. Does the polymer undergo the same photochemical modifications under the two modes of irradiation? To answer that question, in this work, the fate of the matrix was investigated under laser exposure at 405 nm, and the chemical modifications would be followed by in situ infrared spectroscopy and would be compared to the ones obtained under conventional excitation at 365 nm.

Experimental Section

Materials and Film Preparation. Polyacrylamide (PAM) was purchased from Interchim. Ammonium dichromate

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* To whom correspondence should be addressed. E-mail: yael.israeli@univ-bpclermont.fr.

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$(NH_4)_2Cr_2O_7$ (ADC) was supplied by Fluka (purum pro analysis). All of the compounds were used without further purification. All of the starting solutions were prepared in water purified by a Millipore Milli-Q system.

DCPAM films were prepared by the evaporation of a polymer dichromate aqueous solution. The dissolution of the required amount of PAM in deionized, ultrapure water led to a PAM solution which had a 4 wt % PAM composition. To this solution, an exact weight (0.5 wt %) of ADC was then added to obtain the desired chromium weight percentage corresponding to a [PAM unit]/[Cr(VI)] molar ratio equal to 24.5, similar to the one used in dichromated poly(vinyl alcohol).[10] The mixture was stirred to get a homogeneous solution that was poured onto a carefully cleaned Petri dish (diameter = 3.5 cm). The samples were dried in dark chamber under normal laboratory conditions (20 °C and 30−40% relative humidity) for approximately 24 h. After water evaporation, the dry films were pealed off.

To prevent heterogeneous phototransformation in the bulk of the doped polymer film, the incident radiation does not have to be totally absorbed when crossing the whole sample. To meet this condition, the thickness of all of the studied samples corresponded to an absorbance inferior or equal to 1.6 at the irradiation wavelength (365 or 405 nm).

Apparatus and Procedure. A 125 W high-pressure mercury lamp (HPW type, Philips) mainly supplied radiation at $\lambda = 365$ nm (93% at 365 nm and 7% at 334 nm). The source was located along the focal axis of a cylinder with an elliptical base. At the other focal axis, the samples were fixed on a rotating carousel that could receive 15 samples. To absorb the infrared component of the source not filtered by the glass envelope of the lamp, a 1.8 cm thick water Pyrex wall was located between the two focal axes. Experiments were performed at room temperature.

UV−vis spectra were recorded on a Shimadzu UV-2101 PC spectrophotometer equipped with an integrating sphere. Infrared spectra were recorded on a Nicolet 760 Fourier transform infrared spectrometer with Omnic software. Spectra were obtained with a 4 cm^{-1} resolution and 32 scan summation.

For in situ infrared spectra, the films were directly irradiated in the infrared analysis cavity using a DL 100 Toptica laser at 405 nm. By a series of lenses, microscope objectives, and mirrors, the beam laser was focused in the spectrometer cavity, and the power received at the sample position was equal to 2.26 mW cm^{-2} (measured by a EOGENTEC PHSi100 powermeter).

In situ CW-EPR spectra were recorded on a Bruker EMX spectrometer at 9.6 GHz with an ER4104OR Optical Transmission Resonator. The film was placed in a quartz tube and directly irradiated in the EPR cavity. The spectra were recorded during irradiation, unless otherwise noted. Irradiations at long wavelengths were generated with a Hanovia xenon Lamp. They were filtered to deliver radiation centered at 365 nm ($\Delta\lambda = 50$ nm). DPPH [2,2-diphenyl-1-picrylhydrazyl] signal was taken as an internal reference for all of the acquisitions with a g value of 2.0023.

The cross-linking of the samples and the nature of the cross-linking bridges were evaluated by gravimetric measurements of the insoluble fraction both in pure water and in an aqueous solution of ethylene diamine tetraacetic acid (EDTA, 0,10 mol L^{-1}). Irradiated films (∼10 mg) were stirred for 24 h in deionized, ultrapure water (10 mL) or for six days in EDTA solution (10 mL) at room temperature. The insoluble fraction was filtered and dried for 24 h at room temperature until complete water evaporation. The percentage of the dry insoluble fraction (I_f) is defined as follows:

$$I_f = 100 \times M_{insoluble}/M_{initial}$$

where $M_{insoluble}$ is the mass of the insoluble polymer in water or in EDTA solution, and $M_{initial}$ is the mass of the polymer before immersion in water or in EDTA solution.

Results and Discussion

Conventional Irradiation at 365 nm and at Room Temperature. First, the behavior of polyacrylamide (PAM) films in the absence of chromium(VI) was studied under conventional irradiation at 365 nm in order to understand the influence of ammonium dichromate on the physicochemical changes upon exposure. Initially, the polymeric matrix did not absorb between 200 and 800 nm, and no evolution of the UV−visible spectra was observed even after 1600 h of irradiation.

Analysis of changes in the IR spectra resulting from exposure required that the main absorption bands of the spectrum of the polymer free of chromium salt were identified. The main spectral features of PAM are presented in Table 1, according to the literature.[20−22] PAM irradiation did not cause any modification of the IR spectra.

So, polyacrylamide appeared to be stable under irradiation at 365 nm and at room temperature even after 1600 h of exposure.

Evolution of the Absorbing Species upon Irradiation. In UV−vis spectroscopy, DCPAM film presents two absorption bands at 271.5 and 371.5 nm due to the presence of chromium(VI) (Figure 1). Upon conventional excitation, UV−vis spectra evolution revealed a decrease of these two bands indicating a reduction of chromium species (Figure 1). The reduction was also confirmed by infrared spectroscopy with the decrease of the Cr^{VI}−O stretching vibration bands detected at 941 and 877 cm^{-1}. In parallel, the chromium(V) absorption band at 520 nm, evidenced by difference spectra (subtraction: irradiated−nonirradiated), developed and then tended to decrease. However, no bands of chromium(III) was detected even after longer irradiation time.

The kinetics evolution of the absorbance at 371.5 nm, which corresponds to the absorption of both chromium(VI) and chromium(V) is reported in Figure 1 (inset). It seemed that the reduction took place in two successive steps, as in the case of DCPVA:[10] a fast step of reduction of chromium(VI) into chromium(V) during the first 3 h, and a slow step of reduction of chromium(V) into chromium(III) above this irradiation time. The evolution of the absorbance at 941 cm^{-1} against the irradiation time indicated that after 3 h of exposure, more than 70% of chromium(VI) was consumed (Figure 2a). In parallel, from the beginning of irradiation, chromium(V) was quickly formed as shown in Figure 2a. Chromium(V) concentration reached a maximum after roughly 3 h, and the species was then converted into chromium(III).

Chromium(V) was followed by in situ electron paramagnetic resonance spectroscopy. The kinetics evolution obtained in Figure 2b was in agreement with the one observed by UV−vis

TABLE 1: Main Infrared Absorption Bands of Polyacrylamide

| wavenumber (cm^{-1})	assignment
3338	N−H stretching vibration (symmetric)
3195	N−H stretching vibration (asymmetric)
2936	C−H stretching vibration
1665	C=O stretching vibration (amide I)
1450	C−N stretching vibration
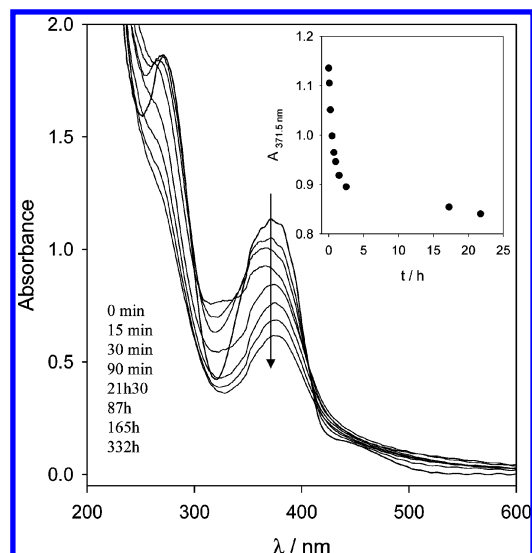
Figure 1. Evolution of the UV−vis spectra of a film (6.94% PAM + 0.5% ADC) upon irradiation at 365 nm at room temperature. Inset: Kinetics evolution of chromium(VI) (band at 371.5 nm).
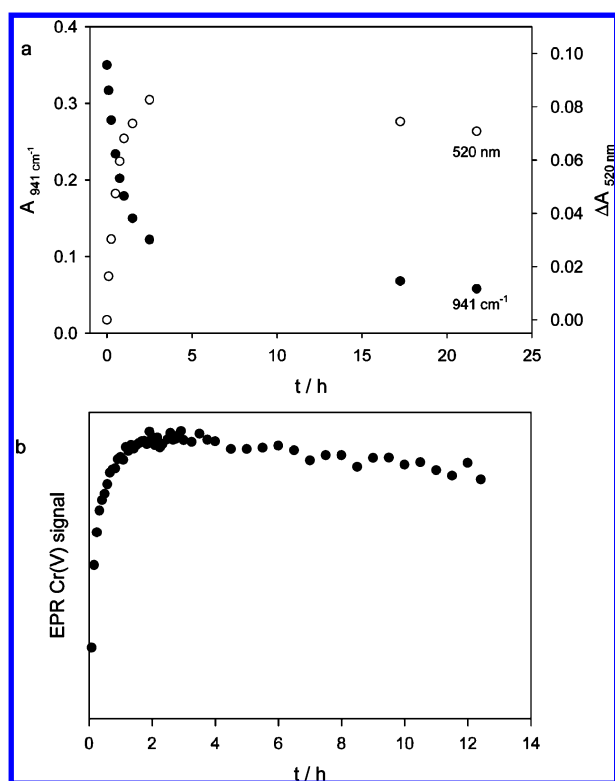

Figure 2. (a) Kinetics evolution of chromium(VI) reduction (band at 941 cm^{-1}) and of chromium(V) formation (band at 520 nm) and (b) evolution of EPR Cr(V) signal upon the exposure of a film (6.94% PAM + 0.5% ADC) at 365 nm and room temperature.

spectroscopy, confirming the reduction of this chromium species. ON−OFF experiments performed on dichromated polyacrylamide revealed that in the dark, chromium(V) was stable in the PAM matrix as shown in Figure 3. Indeed, when the irradiation was on, the EPR Cr(V) signal increased against the irradiation time, but in absence of light, the intensity remained roughly constant. By comparison with previously studied dichromated systems such as dichromated poly(vinyl alcohol),[10] the stability of chromium(V) was due to its ability to bridge the polymeric chains to each other. So one can ask if such a complexation process could also occur in DCPAM. This question will be answered later.
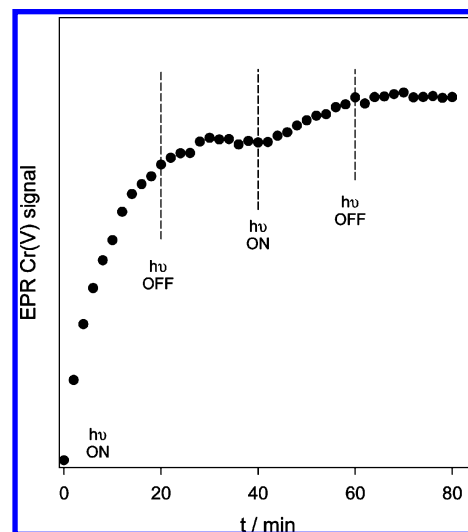

Figure 3. Evolution of EPR Cr(V) signal upon ON−OFF experiments.
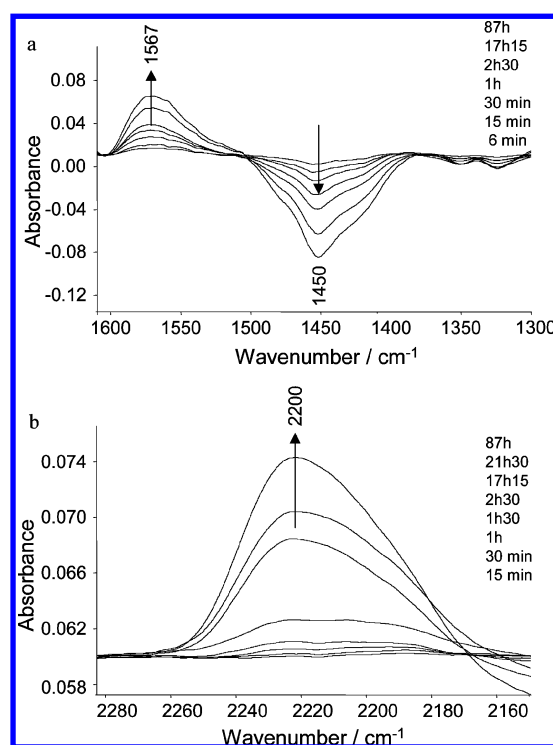
Figure 4. Evolution of the infrared difference spectra of a film (6.94% PAM + 0.5% ADC) upon irradiation at 365 nm at room temperature: (a) in the domain of 1600−1300 cm^{-1} and (b) in the domain of 2280−2160 cm^{-1} (subtraction: irradiated−nonirradiated).

Evolution of the Polymeric Matrix upon Irradiation. Upon exposure at 365 nm, the evolution of the infrared difference spectra of DCPAM films showed some changes specially in the 1600−1300 cm^{-1} and the 2280−2160 cm^{-1} domains (Figure 4) and the 3500−3000 cm^{-1} region (not shown).
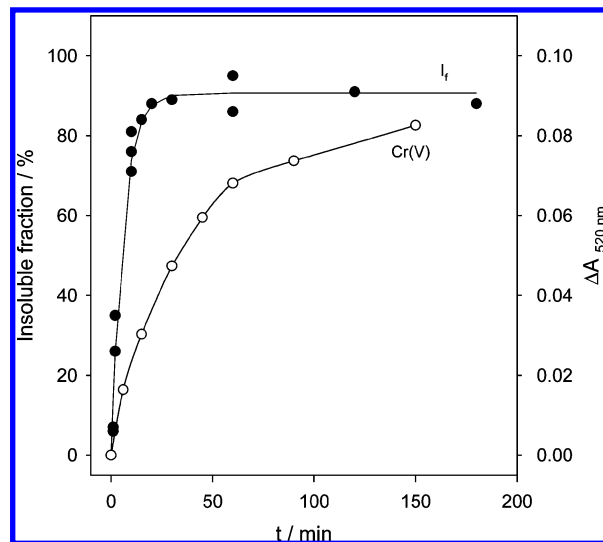
The polymeric matrix underwent some chemical modifications with the formation of two absorption bands at 2220 and 1567 cm^{-1} and with the decay of the C−H stretching vibration band at 3195 cm^{-1} and the C−N stretching vibration band at 1450 cm^{-1} (Table 1). The decrease of the C−H and C−N bonds was linearly correlated with the disappearance of chromium(VI) (Figure 5). This feature highlighted that a loss of the amide group CONH$_2$ occurred during the first step of reduction of chromium(VI) into chromium(V).

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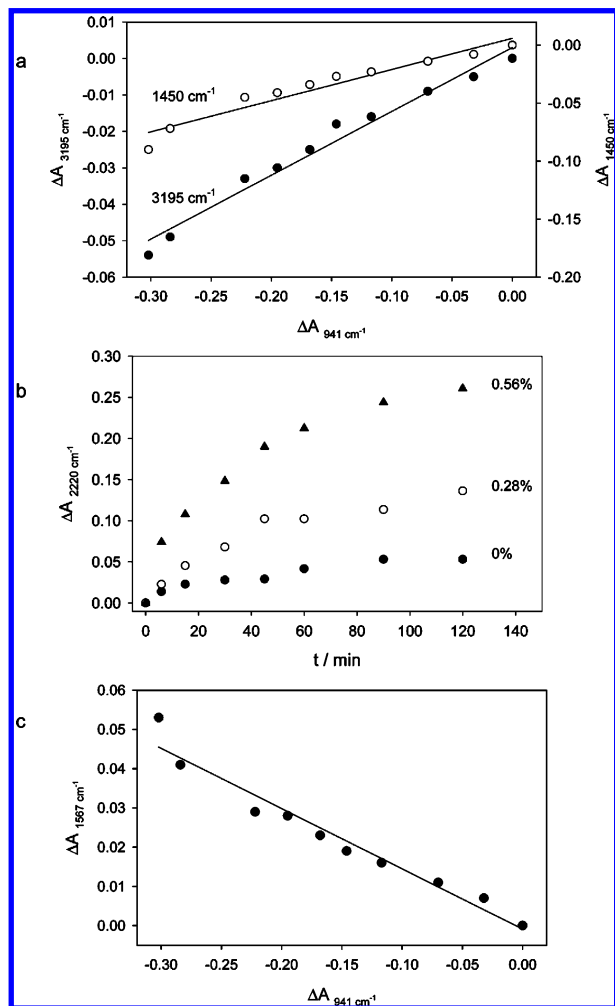
Figure 5. (a) Correlation between the disappearance of N–H (band at 3195 cm^{-1}) and C–N groups (band at 1450 cm^{-1}) and the one of chromium(VI) (band at 941 cm^{-1}); (b) Kinetics evolution of formation of the band at 2220 cm^{-1} upon irradiation at 365 nm of DCPAM films containing various amounts of formamide; and (c) Correlation between the formation of the band at 1567 cm^{-1} and the decay of chromium(VI).

Figure 6. Evolution of chromium(V) formation (band at 520 nm) and of the insoluble fraction in water of a film (6.94% PAM + 0.5% ADC) as a function of the irradiation time at 365 nm at room temperature.

In parallel, a band at 2200 cm^{-1} developed from the beginning of irradiation (Figure 4b). According to the literature,[20,21,23] this band could be assigned to the stretching vibration of the isocyanate group, N=C=O. Moreover, Wu et al. have studied the formamide adsorbed on TiO$_2$ and they have demonstrated that gaseous isocyanic acid, HNCO was formed under exposure at 320 nm.[24] This gas was detected by infrared spectroscopy by its N=C=O vibration band at 2200 cm^{-1}. Thus, to verify that under irradiation at 365 nm, the amide groups of dichromated polyacrylamide led to the formation of isocyanic acid trapped in the polymeric matrix, two experiments were performed.

(1) First, we verified that in our experimental conditions, the irradiation of formamide at 365 nm in a dichromated media allowed the formation of isocyanic acid. For this purpose, a DCPVA film containing the formamide was submitted to exposure. It was shown that under irradiation, no band at 2200 cm^{-1} was developed in a DCPVA film.[10] So if HNCO would form, then this gas would be trapped in PVA matrix. As expected, the irradiation of PVA/ADC/formamide led to the disappearance of the amide group (decrease of the band at 1689 cm^{-1}) and in parallel to the development of the band at 2220 cm^{-1} characteristic of isocyanic acid formation.

(2) In the second experiment, a kinetics study was investigated on two types of films containing constant concentration of PAM (6.94%) and ADC(0.5%) and various concentrations of formamide (0.28 and 0.56%). The kinetics of formation of the band at 2220 cm^{-1} in the two types of films and in a DCPAM film free of formamide are represented in Figure 5b. As shown, the higher the quantity of molecular amide in the medium, the more the absorbance of the band for a given irradiation time and so, the higher the concentration of isocyanate groups was.

These two sets of results confirmed the attribution of the band at 2200 cm^{-1} to the asymmetric stretching vibration of the isocyanate groups NCO and thus the formation of isocyanic acid, HNCO, this acid resulting from the oxidation of the amide groups photoinduced by chromium(VI). Moreover, this gas was formed both in the presence and in the absence of oxygen.
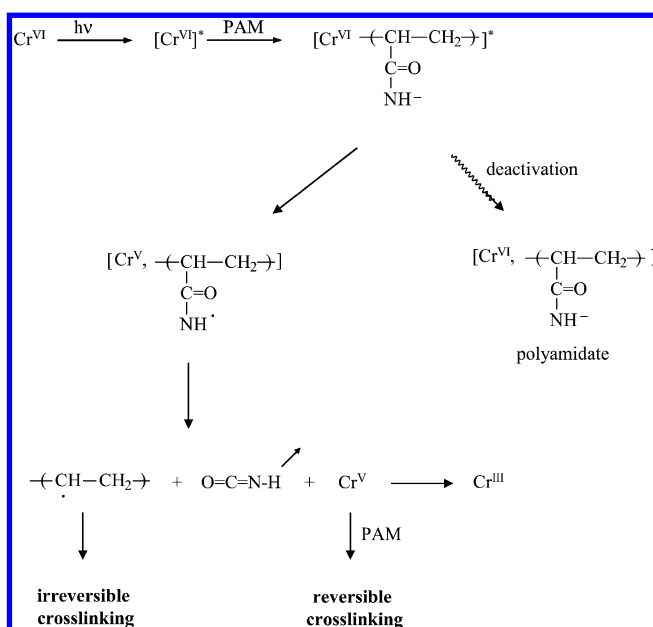
In the same irradiation conditions, the loss of functional groups and the formation of gas have already been observed during the study of dichromated poly(acrylic acid), DCPAA.[11] It was established that under exposure, an acido-basic reaction between chromium(VI) in the excited state and PAA occurred giving rise to the formation of a Cr(VI) carboxylate. Then an intramolecular charge transfer reaction from the carboxylate group to the metallic cation led to the formation of unstable chromium(V) reduced into chromium(III) and of a macroradical ~CH$_2$–C(COO$^•$)H~. This latter underwent a very fast decarboxylation, giving rise to CO$_2$ and to a macroradical.[11] Thus, by analogy with DCPAA, we could assume that a similar photoredox mechanism occurred leading a Cr(VI) polyamidate from which isocyanic acid would be formed.

According to the literature, the C=O vibration band of an amidate group, CONH$^-$ was detected at 1548–1583 cm^{-1}.[25–28] So, the band at 1567 cm^{-1}, which resulted from the transformation of DCPAM, could be assigned to CONH$^-$ groups. The band was linearly correlated with the decrease of chromium(VI) (Figure 5c), indicating that the amidate groups were formed during the first step of reduction of chromium(VI) into chromium(V).

Cross-Linking Process. Insoluble fraction measurements, I$_f$ revealed that DCPAM films initially soluble in water became rapidly insoluble as shown in Figure 6. Indeed, after 1 min of irradiation, the I$_f$ attained a value of 6% and increased by a factor of 5 from two minutes of exposure. A value of 74% was

SCHEME 1: Photoredox Mechanism of DCPAM

Figure 7. (a) Kinetics of chromium(VI) reduction (band at 941 cm^{-1}), amide group decrease (band at 3195 cm^{-1}), and of amidate group formation (band at 1567 cm^{-1}) under laser exposure of a film (6.94% PAM + 0.5% ADC). (b) Correlation between the decrease of amide groups under laser irradiation and the one under conventional irradiation, and between the formation of amidate groups under laser exposure and that under conventional exposure.

obtained after only 10 min. The increasing insolubility was ascribed to a cross-linking of the polymeric matrix.
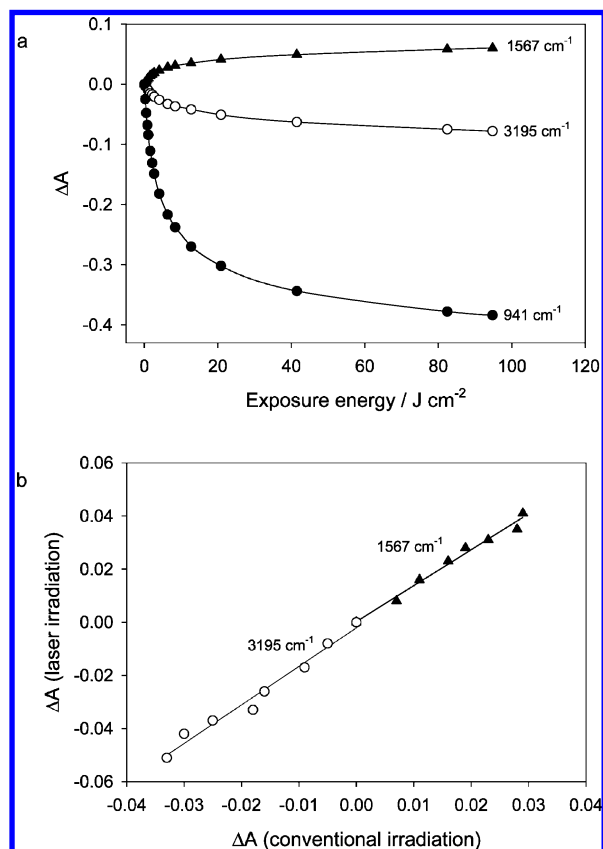
In order to determine the nature of the reticulation, that is to say a chelation process of chromium(V) by the polymeric matrix and/or the formation of covalent bonds between the macromolecular chains, insoluble fraction measurements were performed in EDTA solution, a strong complexing agent toward metallic cation. The immersion of DCPAM films, irradiated for 3 h, for six days in EDTA provoked the decrease of the insoluble fraction from 88% in water to 25% in EDTA. This result pointed out that a complexation process involving chromium(V) occurred. This feature was consistent with the stability of chromium(V) species evidenced by ON−OFF experiments in EPR spectroscopy. The partial solubility revealed that the cross-linking of the polymeric matrix also occurred through the formation of covalent bonds. Such results were confirmed by the evolution of I_f and the concentration of chromium(V) as a function of the irradiation time. Figure 6 showed that the maximum value of I_f was attained after 30 min, whereas the maximum amount of chromium(V) was formed after 3 h.

From the set of results obtained by infrared, UV−vis, and EPR spectroscopy, and by insoluble fraction measurements, a mechanism was put forward (Scheme 1).

Chromium(VI) in the excited state, reacted with the amide groups by an acido−basic reaction to form amidates, after which a charge transfer reaction occurred, leading to the reduction of chromium(VI) into chromium(V) and in parallel the formation of a macroradical $\sim CH_2-C(CONH^\bullet)H\sim$. This latter underwent a homolytic cleavage of the C−C bond of the C−C(ONH$^\bullet$) group, giving rise to the release of isocyanic acid HNCO and the formation of $\sim CH_2-CH^\bullet\sim$. These macroradicals would lead by recombination to covalent bonds, which would be responsible for the irreversible cross-linking of the polymeric matrix, the chelation of chromium(V) by PAM being at the origin of the reversible reticulation. The contribution to the cross-linking process of the macroradicals issued from the abstraction of hydrogen on the tertiary carbon could not be ruled out. The presence of polyamidate observed under exposure resulted from the deactivation of the Cr(VI) polyamidate.

Laser Irradiation at 405 nm and at Room Temperature. Figure 7a represents the evolution of chromium(VI) (band at 941 cm^{-1}) as a function of the exposure energy. It shows that

the kinetics evolution was similar to the one observed under irradiation at 365 nm (Figure 2a). The decreases of the absorbance of the Cr−O band under each type of exposure were linearly correlated (not shown): this feature was in perfect agreement with the fact that the primary process related to the chromium species was similar for the two modes of irradiation.[19]

Concerning the polymeric matrix, similar chemical modifications were observed under conventional and laser irradiation: the decrease of the N−H and C−N bonds (at 3195 and 1450 cm^{-1}, respectively) and the formation of isocyanic acid and amidate groups (at 2220 and 1597 cm^{-1}, respectively). Figure 7a showed that the consumption of chromium(VI) provoked the decrease of the amide groups and, in parallel, the formation of amidates. It was important to note that the evolution of these two groups upon laser irradiation at 405 nm was perfectly correlated with the one under exposure at 365 nm (Figure 7b). So, it could be concluded that whatever the irradiation mode, conventional or laser, the polyacrylamide underwent similar phototransformation. Thus, it is established that, based for the first time on both the fate of chromium(VI) and the polymeric matrix, conventional (365 nm) and laser irradiation (405 nm) lead to similar chemical modifications.

In summary, conventional irradiation at 365 nm appears to be representative of the phenomenon occurring in dichromated material upon laser irradiation.

Comparison DCPAM-DCPVA under Irradiation at 365 nm. To specifically determine the role of the amide groups with respect to the hydroxyl groups in the photoredox process, the

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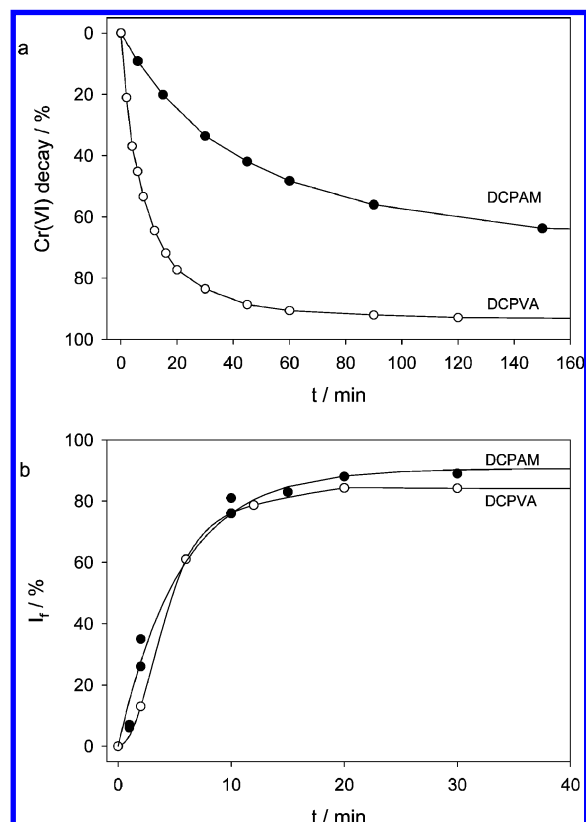
Figure 8. Kinetics evolution upon irradiation at 365 nm at room temperature of DCPAM and DCPVA films of the following: (a) chromium(VI) reduction and (b) of insoluble fraction.

kinetics evolution of chromium(VI) reduction in a film of DCPAM (6.94% PAM + 0.5% ADC) was compared to the one in DCPVA (4.3% PVA + 0.5% ADC) (Figure 8a). In both films, the [polymer unit]/[Cr(VI)] molar ratio was equal to 24.5.

The comparison revealed that the kinetics of chromium(VI) reduction strongly depended on the nature of the polymeric matrix. The initial rate of reduction in DCPAM was roughly 6 times lower than that in DCPVA. Such difference could be explained by the fact that in the two photosensible systems, the photoredox mechanism was different. In dichromated polyacryl-amide, it first involved an acido−basic reaction between the amide groups and chromium(VI) in the excited state, followed by a charge transfer reaction. In DCPVA, only the charge transfer reaction occurred.

In DCPAM and DCPVA, each polymeric matrix underwent some architectural modifications under irradiation. The cross-linking that took place in both photosensitive systems was based on a complexation reaction of chromium(V) by the functions of the macromolecular chains. This chelation was responsible for the stabilization of chromium(V) in the polymer. However, in DCPAM the reticulation also occurred through an irreversible process involving the macroradicals $\sim CH_2-CH^{\bullet}\sim$ formed during the release of isocyanic acid HNCO. The formation of covalent bonds could explain that the initial rate of insoluble fraction in DCPAM was higher than the one in DCPVA (Figure 8b). Indeed, after 2 min of irradiation, I_f attained a value of 31% in DCPAM compared to 13% in DCPVA.

Conclusions

A molecular approach of DCPAM films elucidated that under conventional irradiation at 365 nm, the reduction of chromi-um(VI) took place, leading to chromium(V). Even though a slow chromium(V) decrease was observed by EPR spectroscopy, no chromium(III) could be detected even after long irradiation times. The comparison with DCPVA, for which chromium(III) was observed, showed that the kinetics of chromium(VI) reduction depended on the chemical structure of the polymeric matrix. ON−OFF experiments performed in EPR spectroscopy and insoluble fraction measurements not only evidenced that chromium(V) was stable in PAM matrix but also that it was chelated by the amide groups.

In parallel, the macromolecular approach showed that the polymer underwent chemical and architectural modifications. In particular, during the first step of chromium(VI) reduction, isocyanic acid was formed and trapped in the matrix. This gas resulted from the loss of the amide groups, which gave rise to the formation of macromolecular radicals responsible for the reticulation of the polymer. Thus, this work points out that in DCPAM, the chelation of chromium(V) and the formation of covalent bonds between the macromolecular chains were at the origin of the cross-linking of the PAM matrix. So, in conclusion, as in the case of previously studied dichromated systems, the investigation of a molecular and macromolecular approach allowed understanding of the contribution of the functional group in the photoredox and the cross-linking process in detail.

The same photochemical approach was applied to DCPAM under laser irradiation. For the first time, it was verified that the chemical modifications undergone by the photosensitive material were identical to the ones observed upon conventional irradiation at 365 nm. From this study, it was thus shown that the irradiation at 365 nm was representative of the physico-chemical process occurring upon laser irradiation in such dichromated materials.

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