
**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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**To cite this Article** Israëli, Y. , Frezet, L. and Rivaton, A.(2008) 'Photochemical Processes Involved in a Biopolymer Doped by Chromium(VI) during Hologram Recording', Journal of Macromolecular Science, Part A, 45: 12, 1037 — 1046
**To link to this Article: DOI:** 10.1080/10601320802457840
**URL:** http://dx.doi.org/10.1080/10601320802457840

*Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry* (2008) **45**, 1037–1046

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320802457840

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# Photochemical Processes Involved in a Biopolymer Doped by Chromium(VI) during Hologram Recording

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Received March 2008 and accepted May 2008

This paper is devoted to the study of the photochemical processes occurring during hologram formation in a biopolymer, agar doped by chromium(VI). The evolution of both the absorbing chromium species and the polymer allowed elucidating the reactions taking place during irradiation in conditions representative of hologram formation. As previously observed with dichromated poly(vinyl alcohol) (PVA), polymer containing hydroxyl groups as agar, irradiation of dichromated agar provoked a two step reduction of chromium species and the crosslinking of the host polymer. But agar has a rather complex chemical structure and the photoproducts formed along the polymeric chains throughout the photoredox process were different in agar and in PVA. The photostability of the matrix, that has been proven, coupled with the possibility to record good quality holograms, allowed us to propose dichromated agar as a new natural photosensitive biomaterial.

**Keywords:** dichromated agar, hologram formation, mechanism, crosslinking



## 1. Introduction

Currently, holography is of major interest because of its potential applications in many fields, from optical storage to art. Dichromated polymeric systems (1–4) provide the opportunity to record good quality holograms. Previous studies showed that the primary step involved during hologram formation in dichromated poly(vinyl alcohol) (DCPVA) and dichromated poly(acrylic acid) (DCPAA) was a photoredox process involving a one electron transfer from the polymeric matrix to the metallic cation, giving rise to the formation of a macroradical and to chromium(V) (5–7). The doped matrixes were shown to undergo two processes photoinduced by Cr(VI) reduction: modifications of the chemical structure and crosslinking (8,9). In the case of DCPVA, polymer containing hydroxyl groups as agar, the photoredox process involved two steps:

First, a fast step of reduction of Cr(VI) into Cr(V), accompanied by the oxidation of OH groups of PVA into ketonic functions and the crosslinking of the polymer. The reticulation process involved a complexation of Cr(V) by the macromolecular chains.

Second, a slow step of reduction of Cr(V) into Cr(III) accompanied by the formation of carboxylate functions on the polymeric chains and the chelation of Cr(III) by the macromolecular chains.

In addition, the crucial role played by Cr(V) species was highlighted. It was established that Cr(V) not only was an indicator of the hologram quality, but also appeared to be responsible for the crosslinking involved in the hologram formation.

Other polypeptide systems have been exploited as photosensitive materials (10,11) and a class of holographic materials based on polysaccharides was developed (12–16). For example, in the case of dichromated cellulose triacetate, Wang et al. (15) showed that upon light exposure, Cr(VI) was reduced into Cr(III) through Cr(V) formation and that the polymer underwent chain scissions. A three dimensional network was formed in the exposed regions resulting from the crosslinking by Cr(III) of the shorter molecular chains issued from the scission of the longer chains of dichromated cellulose triacetate (15).

Agar produced by seaweeds is a natural polysaccharide containing hydroxyl groups as gelatin and PVA. Agar is well known in biology and in the food industry, but no holographic results were reported in the literature. Thus, recently we have investigated a holographic approach consisting in optimizing the chemical and physical parameters in order to record good quality holograms. It was shown that agar doped with dichromated ammonium could be

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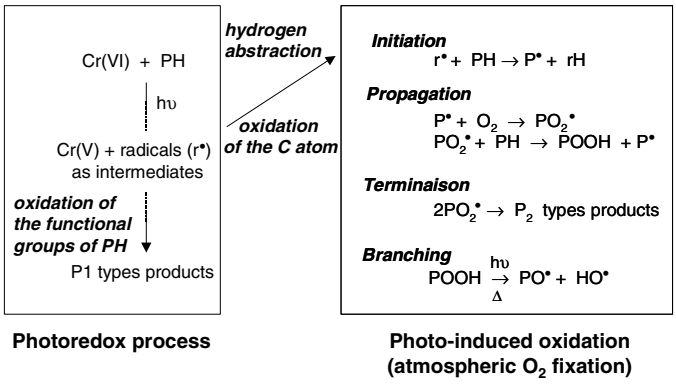



**Sch. 1.** Photoredox process of dichromated systems and photo-induced oxidation of polymers.

considered as a new light sensitive material for real time holographic recording (17). Diffraction efficiency measurements allowed to conclude that the optimal composition was 3.0% agar and 0.40% ADC corresponding to a [agar unit]/[[Cr(VI)] molar ratio of 3.1 (17).

Agar has a rather complex chemical structure with sulfate groups and ether bonds besides OH groups. A major problem associated with the applications of polyethers is their instability to long wavelengths exposure ($\lambda > 300$ nm). Despite the fact that aliphatic polyethers do not absorb radiation of wavelengths longer than 300 nm, these polymers are known to be very sensitive to photooxidation. The degradation can be initiated by chromophoric defects (X) which absorb UV light and produce radicals ($r^\bullet$) which further react with the polymer (PH) by hydrogen abstraction on the polymeric backbone. The macroradicals produced ($P^\bullet$) further react with oxygen, leading to peroxy radicals and hydroperoxides by abstraction of a labile hydrogen atom. This oxidation process is auto-catalyzed due to the thermal and photochemical instability of hydroperoxides furnishing two radicals. The various sequences of the photo-induced oxidation of polymers are reported in Scheme 1 (18).

The high photosensitivity of polyethers to UV induced oxidation resulted from the oxidizability of the carbon atoms in $\alpha$-position to the oxygen atom (19).

It was therefore necessary to complete the holographic approach carried out on dichromated agar by a photochemical one in order to answer the following questions:

1. Are the mechanisms of holograms formation the same as those involved in PVA, due to the presence of OH groups in both polymers?
2. Does agar undergo a photo-induced oxidation (fixation of atmospheric $O_2$) under exposure? In other words, it must be determined if the radicals involved in the photoredox process of dichromated agar upon exposure could be able to initiate the photodegradation of agar without further involvement of Cr species.

With this aim in view, the paper was focused on the physical-chemical changes of both the photoactive chromium species and the polymeric matrix occurring upon exposure at 365 nm. Under such irradiation conditions, the primary processes were similar to those involved during hologram formation under laser excitation (488 or 514 nm). A combination of analytical techniques, UV-visible (UV-vis), Electron Paramagnetic Resonance (EPR) and Infrared (IR) spectroscopy associated to chemical derivatization treatments, was used to follow the fate of both the absorbing species and the polymer. The crosslinking process was monitored by microhardness measurements. In addition, the photostability of non-doped agar films was investigated.

## 2. Experimental

### 2.1. *Materials and films preparation*

Agar (granular agar) was purchased from Difco. It was characterized by a gel-setting temperature around 40°C and a gel-fusion temperature in the 90–120°C range (20). Ammonium dichromate (ADC) (purum p.a.) was supplied by Fluka. All the compounds were used without further purification.

Dichromated agar films were prepared by the evaporation of a polymer dichromate aqueous solution. The solution was obtained by the dissolution of the required amount of agar in preheated, de-ionized, ultra pure water (ca 90°C) to obtain an agar solution, the composition of which was 3.0 wt% agar. Due to the gelling property of agar and consequently, to avoid a highly viscous polymer solution, it was then necessary to double the water quantity. After that, the solution was cooled and maintained at a constant temperature of 45°C to avoid gel formation. An exact weight of ADC was then added to the solution to obtain the desired chromium weight percentage (e.g., 0.40% ADC) corresponding to a [agar unit]/[Cr(VI)] molar ratio equal to 3.1 (17). This ratio, with an excess of polymer towards the Cr(VI) photosensitive species, was necessary to get good-quality holograms (17). The mixture was stirred to get a homogeneous solution and 1.00 mL was poured onto a carefully cleaned Petri dish (diameter = 5.5 cm) pre-heated at 45°C. The samples were dried in a dark chamber under normal laboratory conditions (20°C and 30–40% relative humidity) for approximately 24 h. After water evaporation, dry films (8–10 $\mu$m) were peeled 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 the studied samples was lower than 10 $\mu$m, which corresponded to an absorbance inferior or equal to 1.6 at the irradiation wavelength (365 nm). Agar films, free of chromium salts, were prepared with the same procedure.

### 2.2. *Apparatus and procedure*

A 125-W high-pressure mercury lamp (HPW type, Philips) mainly supplied radiations 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 water borosilicate wall 1.8 cm thick was located between the two focal axes. Experiments were performed at room temperature.

Irradiations at long wavelengths ($\lambda > 300$ nm) were realized using a SEPAP 12/24 unit providing an artificial ageing corresponding to medium accelerated conditions. This chamber is made of a square reactor equipped with four medium-pressure mercury lamps (Mazda MA 400) situated in vertical position at each corner of the chamber. In the center of the chamber, the samples were fixed on a rotating carousel of 13 cm of diameter which can receive 24 samples. In this series of experiments, the temperature at the surface of the samples was fixed at 60°C.

*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 the acquisitions with a g value of 2.0023.

UV-visible 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 scans summation.

The identification of most of the photoproducts formed in the polymer films was made by using chemical derivatization treatments that selectively convert photoproducts into groups with different infrared absorption. Irradiated films were exposed to $NH_3$ gas at room temperature in a flow Teflon reactor that had to be sealed off to permit the reaction to proceed. In the case of HCl treatment, the sample was placed in an atmosphere saturated with HCl vapor. $NH_3$ reacts with esters and carboxylic acid groups to give amides and ammonium carboxylates, respectively; aldehydes and ketones are transformed into imines. Carboxylate groups react with HCl to give the corresponding carboxylic acids.

Microhardness measurements were performed on a Micromet 2100 Buehler apparatus. In the Knoop hardness test, a diamond indenter, in the form of a rhombic-based pyramid with angles $\alpha$ (172.5°) and $\beta$ (130°) between the opposite edges at the vertex, was pressed into the surface of the material using a prescribed force F (200 N). After the force was removed, the length of the longer diagonal of the resulting indentation, d (in mm) was measured. The Knoop hardness, HK value was calculated according to the relation:

$$HK = 1.451 \times \frac{F}{d^2}.$$

## 3. Results and discussion

### 3.1. *Polymer characterization*

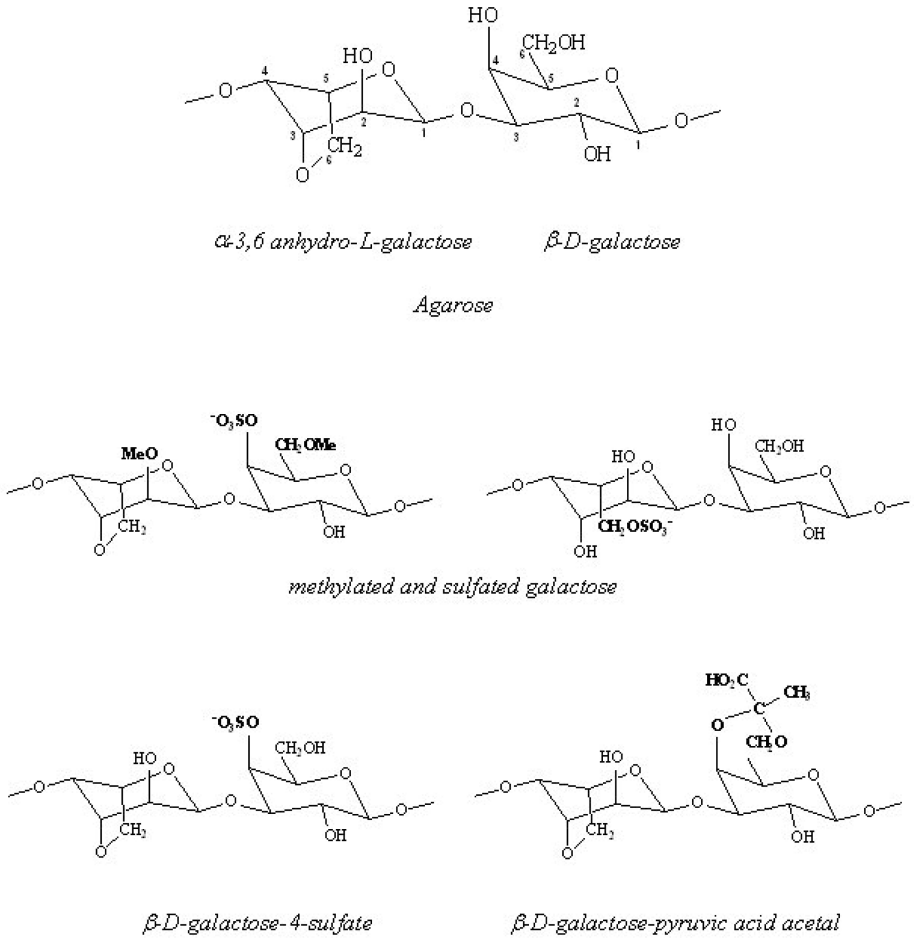
Agar is a natural polysaccharide containing agarose and agaropectin units (21–24). Agarose is a neutral polysaccharide resulting from the repetition of disaccharide agarobiose or neo-agarobiose. The linear backbone is constituted of alternating three-linked $\beta$-D-galactose and four-linked $\alpha$-3,6-anhydro-L-galactose (Scheme 2). The gelling property of agar is related to agarose. Agaropectin is usually a charged polysaccharide, for which some hydroxyl groups have been substituted by ester sulfate, methyl groups or pyruvic acid acetal. Examples of agaropectin structures are reported in Scheme 2.

Analysis of changes in the IR spectra resulting from exposure requires that the main absorption bands of the spectrum of the polymer free of chromium salt are identified. The main spectral features of agar are presented in Table 1 according to the literature (23, 25–30).

### 3.2. *Evolution of the absorbing species upon irradiation*

Upon exposure at 365 nm, Cr(VI) absorption band at 372 nm was rapidly consumed (Fig. 1). In parallel, a band at 522 nm attributed to Cr(V) species developed (31). The broader band observed to develop at 585 nm when irradiation duration was longer than 25 h was attributed to Cr(III) species (31). The decrease of the IR band at 933 $cm^{-1}$, characteristic of the $Cr^{VI}$—O bond, confirmed the rapid Cr(VI) reduction process.

Kinetics evolution of the UV and IR bands of Cr species (Fig. 2) indicated that the reduction of Cr(VI) took place in two successive steps as in the case of dichromated gelatin (31) and PVA (8). The evolution of $Cr^{VI}$—O bond vibration at 933 $cm^{-1}$and of the Cr(V) band at 522 nm against irradiation time indicated that a first fast step of reduction of Cr(VI) into Cr(V) occurred roughly during the first 60 min of exposure corresponding to 84% of Cr(VI) reduction. Then, the absorbance of the UV band of Cr(V) at 522 nm progressively decreased due to the conversion Cr(V) $\rightarrow$ Cr(III) as evidenced by the development of the Cr(III) band at 585 nm. This slow reduction step of Cr(V) into Cr(III) lasted during several days.




**Sch. 2.** Agarose and examples of agaropectin structures.



We have compared the rate of reduction of Cr(VI) in PVA and in agar: both dichromated films corresponded to the best holographic responses and exhibited before exposure the same Cr(VI) UV absorbance. Kinetics results based on IR analysis (Fig. 3) showed that the initial rate of Cr(VI) → Cr(V) reduction was in the same order of magnitude in both photosensitive systems.

Results deduced from UV and IR analyses were confirmed by EPR spectroscopy. Before exposure three peaks at g values 1.9881, 1.9837 and 1.9792 were observed and attributed to thermal Cr(V) species. Upon *in situ* irradiation, the intensity of these peaks increased (Fig. 4a) confirming the formation of photochemical Cr(V) resulting from the photoreduction of Cr(VI). The oxidation of sugar by Cr(VI) in solution, with an excess of sugar towards Cr(VI), was reported in the literature (32–35) demonstrating that in such conditions, the reduction proceeded according to Cr(VI) → Cr(III) and Cr(VI) → Cr(V) → Cr(III) paths, aldonic acid accompanying Cr(III) species formation. The formation of five- and six-coordinate oxochromate (V) intermediates was reported, the latter requiring stronger acid conditions. Such Cr(V) intermediates were detected at g values around 1.98 whatever the sugar. The observed signals were explained by the involvement of a 1,2–diolate moiety, vicinal hydroxyl groups of sugars, or a 1,2,3-triolate moiety in the binding process of Cr(V) (32–35). These Cr(V) complexes were so stable that they remained in solution several days. Thus, upon *in situ* exposure of dichromated agar, the peaks observed at g values ranging from 1.979 to 1.988 suggested the formation of five-coordinate oxochromate (V) complexes resulting mainly from the binding of Cr(V) by the hydroxyl groups of agarose and/or agaropectin units. Moreover, the stabilization of Cr(V) inside the polymeric matrix when the light was off (Fig. 4b) pointed out the formation of a complex between Cr(V) species and mainly OH groups as observed in the case of DCPVA (8). So, this stabilization evidenced by EPR spectroscopy (Fig. 4b) and the holography-photochemistry correlation obtained by on-off experiments (17) permitted us to conclude that Cr(V) species formed in dichromated agar were an indicator of the holograms quality as in the case of DCPVA.

The absorbance of the two vibration bands at 1425 and 3047 $cm^{-1}$, characterizing the ammonium cations, decreased upon exposure. The decrease only occurred during the first step of reduction of Cr(VI) as confirmed by the linear correlation between the band at 1425 $cm^{-1}$ (N—H

**Table 1.** The main IR absorption bands assignment of agar

| *Wavenumber/cm$^{-1}$* | *Assignment* |
|---|---|
| 3416 | O—H stretching vibration |
| 1616 | C=O stretching vibration of the pyruvate residue in a ketal linkage to the 4- and 6-positions of the galactose unit |
| 1373 | ester sulfate |
| 1075 | C—O—C stretching vibrations of the glycosidic linkage |
| 933 | vibration of the C—O—C bridge of 3–6 anhydrogalactose residues |
| 740 and 770 | skeletal bending of the galactose ring |

deformation vibration) and the one at 933 cm$^{-1}$ (Cr(VI)—O bond) (not shown). Such result might be explained by the conversion of $NH_4^+$ into $NH_3$ resulting from some interaction between the starting $NH_4^+$ and Cr(VI) in the excited state as suggested in the case of DCPVA (8).

### 3.3. *Phototransformation of the host matrix*

The modifications of the chemical structure of the polymeric matrix occurring in parallel to Cr(VI) reduction steps were analyzed by IR spectroscopy.

In the 1800–1500 cm$^{-1}$ domain, the development of a broad band with maxima at 1736 and 1618 cm$^{-1}$ accompanied by a shoulder at 1577 cm$^{-1}$ was observed for short irradiation durations (below 150 min) (Fig. 5). After a hundred hours of irradiation, corresponding to the second reduction step Cr(V) → Cr(III), the band at 1577 cm$^{-1}$ became

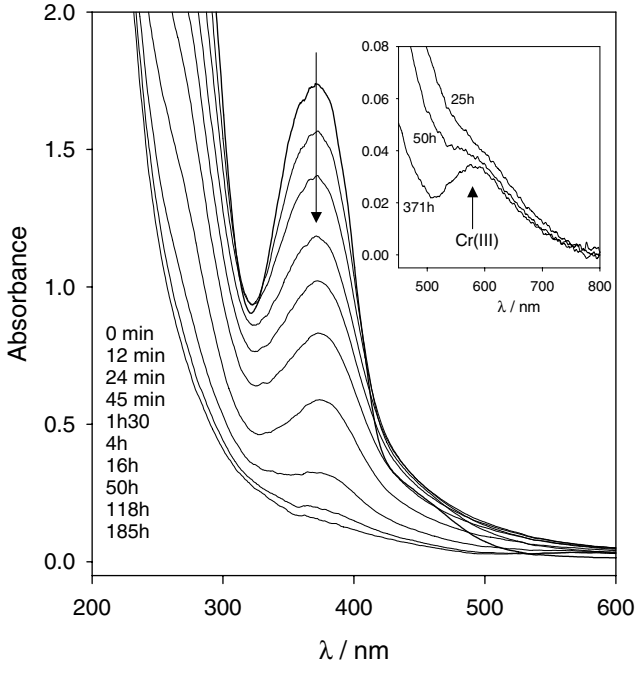



**Fig. 1.** Evolution of the UV-visible spectra of a film (3% agar and 0.40% ADC) upon exposure at 365 nm and at room temperature. Insert: Evolution of Cr(III) band at 585 nm upon irradiation.

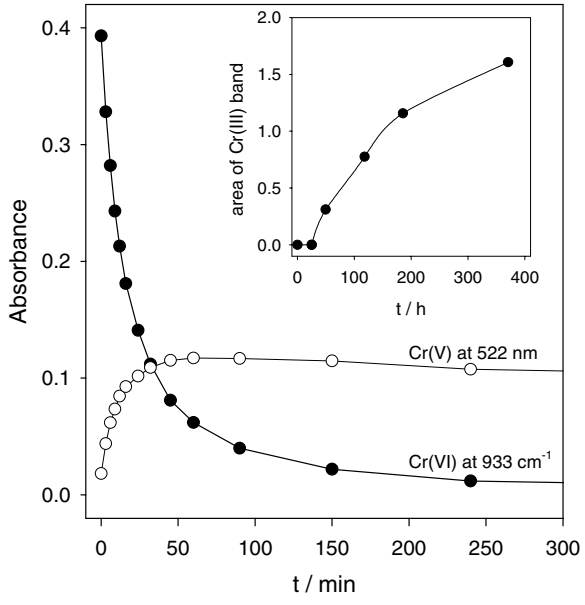



**Fig. 2.** Kinetics evolution of Cr(VI) (933 cm$^{-1}$) and Cr(V) (522 nm) upon exposure at 365 nm and at room temperature. Insert: Evolution of the area of the Cr(III) band at 585 nm as a function of the irradiation time.

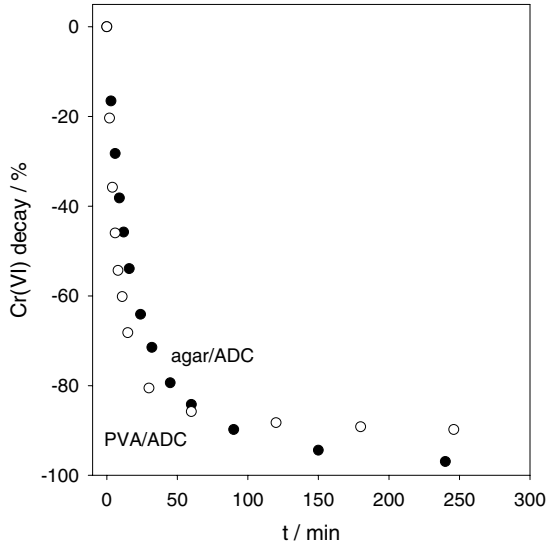



**Fig. 3.** Kinetics of Cr(VI) decay in agar/ADC (band at 933 cm$^{-1}$) and in PVA/ADC (band at 931 cm$^{-1}$).

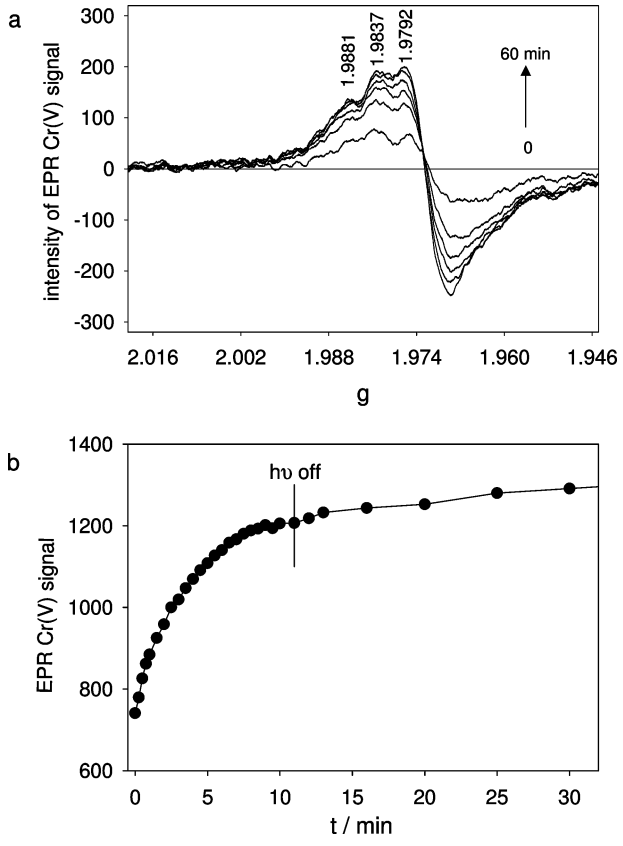



**Fig. 4.** (a) Evolution of EPR difference spectra (subtraction: irradiated—nonirradiated) upon *in situ* irradiation at 365 nm and at room temperature of a film (3% agar and 0.40% ADC). DPPH with a g value of 2.0023 was used as an internal reference. (b) On-off experiment carried out on a film (3% agar and 0.4% ADC): evolution of chromium (V) signal by *in situ* EPR spectroscopy.

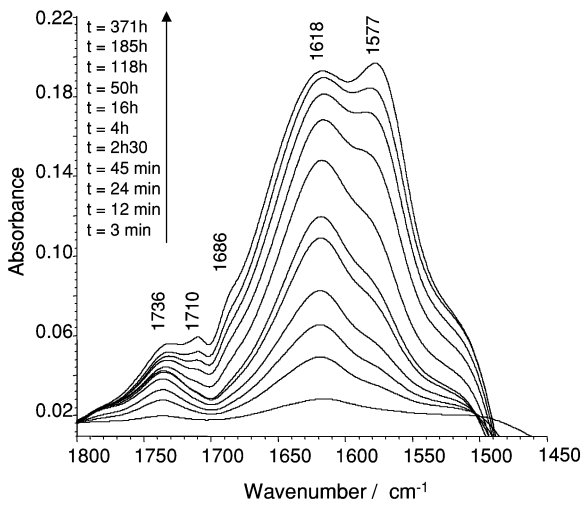



**Fig. 5.** Evolution of the difference IR spectra in the 1800–1450 $cm^{-1}$ carbonyl domain upon exposure at 365 nm and at room temperature of a film (3% agar and 0.40% ADC) (subtraction: irradiated—nonirradiated).

pre-eminent and two shoulders at 1710 and around 1686 $cm^{-1}$ developed.

The nature of the main species resulting from the oxidation of the polymeric matrix was determined by chemical derivatization treatments.

$NH_3$ treatments carried out on irradiated films led to a complete decrease of the band at 1736 $cm^{-1}$ and to the formation of a main absorption band at 1608 $cm^{-1}$ accompanied by a weaker band around 1680 $cm^{-1}$ (Fig. 6a). These vibrations respectively correspond to the carboxylate ions band, obtained by the neutralization of carboxylic acids, and to imines, resulting from the reaction of aldehydes/ketones with $NH_3$.

The absorbance of the band at 1736 $cm^{-1}$ increased rapidly from the beginning of exposure and reached then a plateau. The development of the band at 1736 $cm^{-1}$ occurred during the first Cr(VI) $\rightarrow$Cr(V) reduction step as shown by the linear correlation between the formation of this band and the decrease of the one of Cr(VI) at 933 $cm^{-1}$ (Fig. 7a).

It was then possible to conclude that during the first step of Cr(VI) reduction, the development of the band at 1736 $cm^{-1}$ was related to the formation of carboxylic acid as a main product accompanied by aldehydes/ketones.

HCl treatment carried out on irradiated films led to the decrease of the band at 1618 $cm^{-1}$ and to the formation of a band at 1736 $cm^{-1}$ (Fig. 6b). From these results, the functional group absorbing at 1618 $cm^{-1}$ was attributed to carboxylate species. This attribution was confirmed by $NH_3$ treatment of an agar film doped with glucuronic acid ($C_6H_{10}O_7$) leading to the formation of carboxylate also observed around 1618 $cm^{-1}$. Carboxylate groups were formed during the two steps of reduction of chromium species. Indeed, the development of the band at 1618 $cm^{-1}$ was linearly correlated with the decrease of the one at 372 nm associated to the absorption of both Cr(VI) and Cr(V) species (Fig. 7b).

The band at 1577 $cm^{-1}$ which developed under exposure was not reactive by acidic and basic treatment. This IR frequency, associated with its non-chemical reactivity, could fit with the enol vibration of $\beta$ dicarbonylated-species. Indeed, when a methylene group separates two C=O groups, the molecule can exist in keto- or enol form. The enol form favors the establishment of intramolecular hydrogen bonds and thus, the vibration is observed at low wavenumbers in the range 1538–1640 (36,37). So, the vibration at 1577 $cm^{-1}$ could be tentatively assigned to $\beta$-dicarbonylated-species in the enol form, which mainly developed during the slow reduction step Cr(V) $\rightarrow$ Cr(III).

From the set of results related to the evolution of - i) the absorbing chromium species, - ii) the polymeric matrix and - iii) the identification of the photoproducts, a mechanism was put forward (Scheme 3). The mechanism is illustrated on the $\beta$-D galactose units of agarose in Scheme 3.

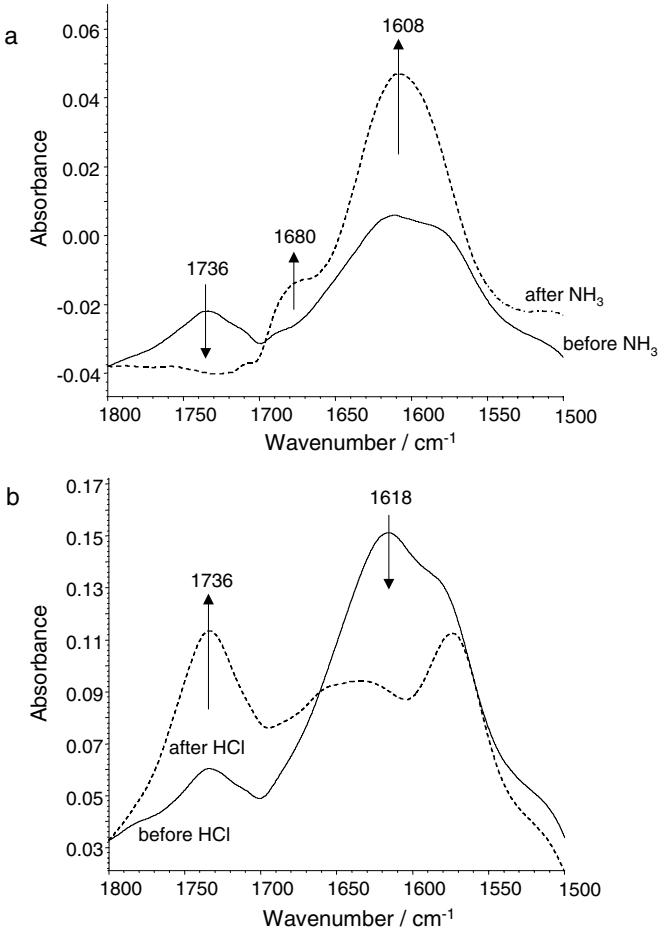



**Fig. 6.** Evolution of the difference IR spectra in the 1800–1500 $cm^{-1}$ carbonyl domain: (a) after $NH_3$ treatment (1 h 15 min) of a dichromated agar film irradiated 2 h 30 min and (b) after HCl treatment (24 min) of a dichromated agar film irradiated 21 h at 365 nm and at room temperature.

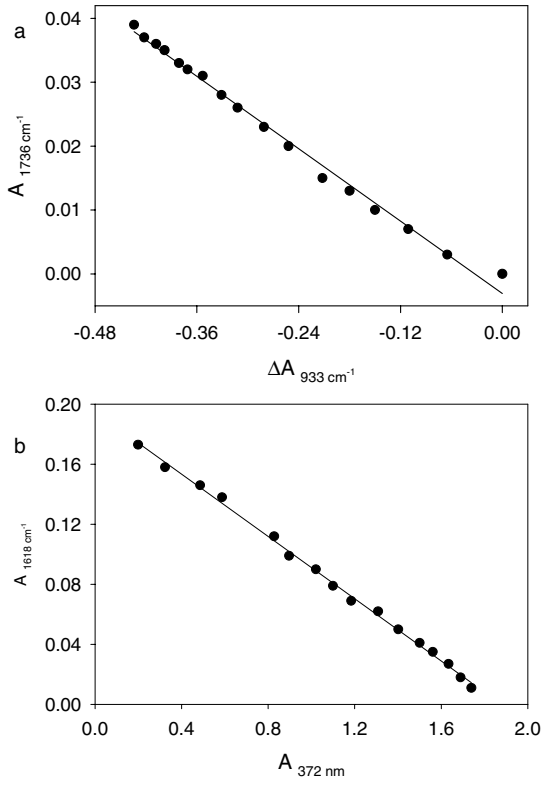
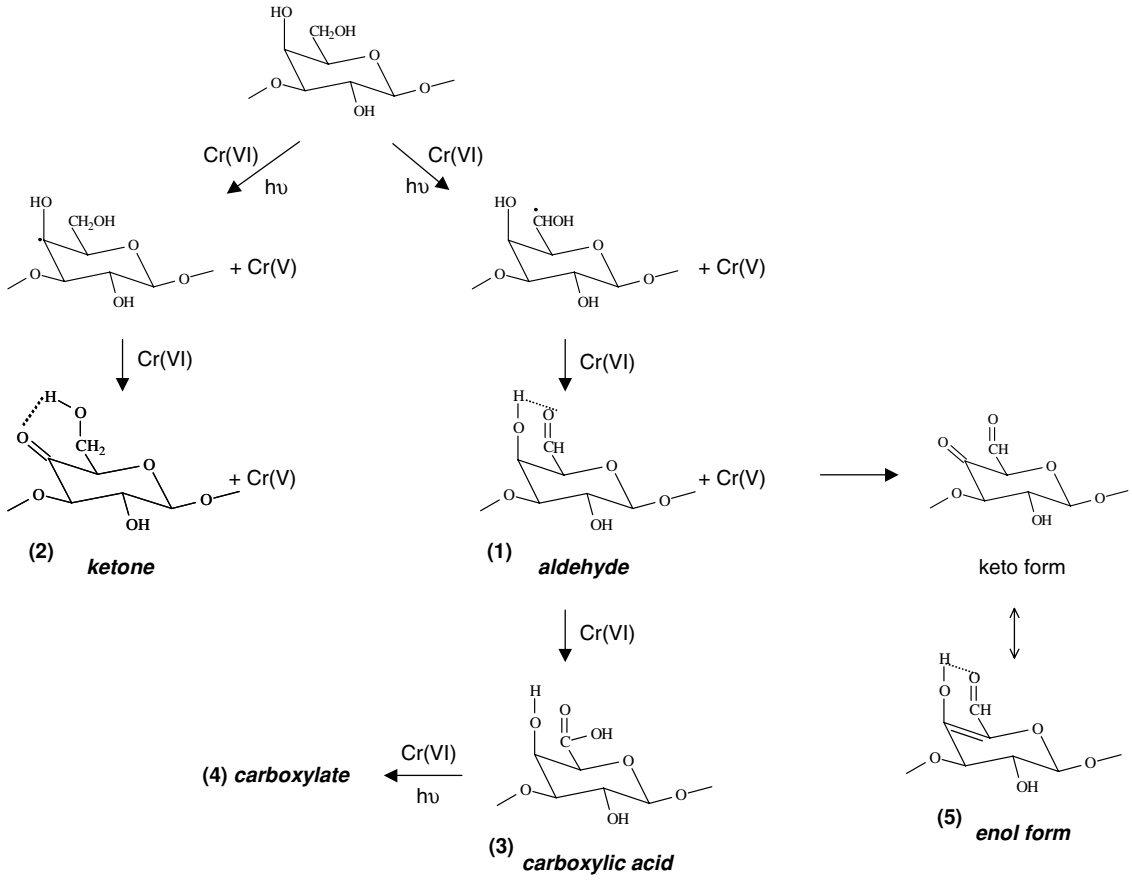



**Fig. 7.** (a) Correlation between carbonyl species formation (at 1736 $cm^{-1}$) and Cr(VI) disappearance (at 933 $cm^{-1}$); (b) correlation between carbonyl species formation (at 1618 $cm^{-1}$) and chromium species disappearance (at 572 nm).

Agar contains primary and secondary alcohols, in $\beta$-position for some of them. The oxidation of primary and secondary alcohols is known to give aldehydes and ketones respectively (34). In doped agar, $\beta$-hydroxy-aldehydes (1) and $\beta$-hydroxy-ketones (2) would be formed. The presence of aldehydes/ketones was evidenced by $NH_3$ treatment. These species participated to the development of the broad band centred at 1736 $cm^{-1}$ which occurred from the beginning of exposure. According to the literature (36,37), the C=O bond vibration of $\beta$-hydroxy-keto groups can undergo a shift to shorter wavenumber by formation of intramolecular hydrogen bonds (36,37). Consequently, the IR bands at 1710 and 1686 $cm^{-1}$ which were observed after long duration of exposure could be assigned to aldehyde (1) and ketone (2) species, respectively, with intramolecular bond with $\beta$-OH groups.

$NH_3$ treatment also evidenced the presence of carboxylic acid as a main photoproduct absorbing at 1736 $cm^{-1}$. It is well known that aldehydes can be easily oxidized into carboxylic acids (38). So, aldehydes (1) formed in agar would be rapidly transformed into carboxylic acids (3). Moreover, it is worth noting that carboxylic acids were formed only during the first reduction step Cr(VI) → Cr(V). In dichromated polyacrylic acid (DCPAA), it was shown that an acido-basic reaction occured between Cr(VI) in its excited state and carboxylic functions leading to the formation of a carboxylate of Cr(VI) (9,39). Thus, by analogy with DCPAA, the formation of the carboxylates (4) observed at 1618 $cm^{-1}$ could be explained by an acido basic reaction involving the carboxylic groups (3).

Once $\beta$-hydroxy-aldehydes (1) and $\beta$-hydroxy-ketones (2) were formed during the Cr(VI) → Cr(V) reduction step, the oxidation of the $\beta$-hydroxyl groups could occur, leading to the formation of ketones in $\beta$-position to aldehydes (5) and *vice versa*. These $\beta$-dicarbonylated species identified to be responsible for the development of the band at 1577 $cm^{-1}$ became pre-eminent for long irradiation duration corresponding to the Cr(V) → Cr(III) reduction step. The formation of these compounds would result from the oxidation of alcohols by Cr(V) (40).




**Sch. 3.** Photoredox mechanism of the $\beta$-D-galactose units of agarose.

### 3.4. *Involvement of atmospheric oxygen in the photochemical processes*

As recalled in the introduction section, polyethers are highly photosensitivities to UV induced oxidation due to the oxidizability of the carbon atoms in $\alpha$-position to the oxygen atom. In agar, carbon atoms in $\alpha$ position to ethers are tertiary and it is well-known that the lability of hydrogen atom on tertiary carbon (agar) is higher than that on secondary carbon (PEO). So, it was of first importance to know if agar also is a photo-instable matrix and if all the modifications of the chemical structure of the polymer were due to a photoredox process implying the oxidation of the OH groups of the polymer. Some of the modifications could result from a fixation of atmospheric oxygen by the macroradicals formed by abstraction of the labile hydrogen atoms of the matrix (18). To answer these questions, two types of experiments were carried out.

1) non doped agar was irradiated at 365 nm. No photooxidation of the matrix was observed even after 2000 h of exposure at 365 nm, despite the fact that ethers are known to be very easily photooxidizable. The explanation could be that the pure sample contains no chromophoric defects able to absorb the photons at such long wavelength.
2) So in a second experiment, non-doped agar was irradiated with polychromatic light at $\lambda > 300$ nm in the SEPAP 12/24 unit. The device is designed to study the photo-aging of polymers in artificial accelerated conditions ($\lambda > 300$ nm). The main changes in the infrared spectra were observed in the carbonyl region with the formation of a broad band at 1730 $cm^{-1}$ and a shoulder at 1777 $cm^{-1}$. Firstly, agar exhibited an important photostability compared to others polyethers: PEO was totally degraded after 20 h of exposure in the same device. Indeed, to observe the same quantity of carbonylated compounds, resulting from the fixation of atmospheric oxygen, the exposure duration for agar was a hundred times higher than that for PEO. The photostability of agar could be attributed to a very low diffusion of oxygen throughout the polymer film. This was confirmed by the fact that for a given irradiation time, the same quantity of photoproducts was formed in agar films of different thickness. This non-observation of the Beer Lambert's law revealed that the photooxidation of agar was heterogeneous and limited to the surface in contact with oxygen. Indeed, the most widespread cause of heterogeneity observed at the macroscopic level in exposed films results from oxygen diffusion-limited effects. Secondly, the comparison of the IR spectra of agar and

doped agar revealed that in both media, the photoproducts formed were totally different. It highlighted that the photoproducts formed in the doped film were only associated to the photoredox process. It means that the radicals formed in the photoredox process were not able to induce a photooxidation of the matrix due to the very low diffusion of oxygen.

When the irradiation of doped agar at 365 nm was performed in a tube sealed under vacuum, the infrared and UV-visible analysis revealed the same features as those evidenced when the exposure was carried out at ambient air. This result confirmed that the atmospheric oxygen did not participate to the photoredox reactions.

### 3.5. *Modification of the architecture of doped agar under irradiation at 365 nm*

As PVA, agar mainly contains hydroxyl groups, and it was established that irradiation of dichromated PVA provoked the polymer reticulation through coordination bonds around Cr(V) which acted as a bridge between the polymeric chains (8). Consequently, one can ask if the biopolymer also undergoes a crosslinking process. The progressive formation throughout irradiation of 3-D network was expected to generate modifications of the mechanical properties of the material. The variation of mechanical properties such as hardness could be probed by Knoop microhardness HK tests. The kinetics evolution of HK upon exposure, presented in Figure 8 showed that HK values were multiplied by 2 after 10 min exposure. Then, the microhardness tended to reach a plateau. It was concluded that the changes in Knoop hardness highlighted a reticulation process which occurred from the beginning of irradiation.

Furthermore, it is worth recalling that on one hand, the evolution of HK and Cr(V) species were similar (Figures 2 and 8) and, that on the other hand, both HK and Cr(V) concentration reached a maximum value, whereas no Cr(III) was formed as evidenced by EPR spectroscopy. Such features suggest that Cr(V) was involved in the matrix crosslinking process as in the case of dichromated PVA. This assumption was consistent with the fact that (i) Cr(V) was stabilized in the polymeric matrix as underlined by on-off experiments performed both in holography and in EPR spectroscopy (17), (ii) the observation of three peaks by EPR spectroscopy upon *in situ* irradiation suggested the formation of five-coordinate oxochromate (V) complexes and (iii) that the hologram conserved its properties without no changes after recording (17). Consequently, according to the results obtained in this work, it could be concluded that agar underwent a reticulation process involving a chelation of Cr(V) mainly by the hydroxyl functions of the polymer. In Figure 8, we reported also the monitoring of DCPVA crosslinking evidenced by the formation of an insoluble fraction. As for the reduction of Cr(VI) (Fig. 3), the kinetics evolutions of doped agar and PVA were roughly similar. For DCPVA films, EDTA treatments allowed us to conclude that Cr(V) act as a bridge between the polymeric chains (8). As it was not possible to carry out this experiment for dichromated agar due to gel formation in aqueous solution at room temperature, the participation of covalent bonds between macromolecular chains in the crosslinking process could not be ruled out.

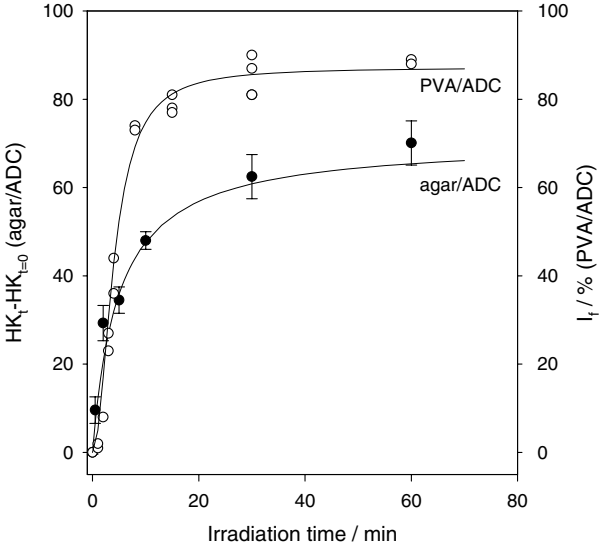



**Fig. 8.** Kinetics evolution of the Knoop harness, HK (F = 200 N), and of the insoluble fraction, $I_f$, respectively measured for agar/ADC and PVA/ADC films upon irradiation at 365 nm and at room temperature.

## 4. Conclusions

In a recent holographic study (17), it was demonstrated that dichromated agar could be a promising photosensitive biomaterial for recording real time holograms. Thus, in order to have a further insight of the mechanism of the hologram formation, a combined polymer/chromium approach reported in this paper was carried out.

Upon irradiation at 365 nm, conditions representative of the holographic recording, the polymer undergoes a modification of the chemical structure photo-induced by the photoactive species. The same two-step reduction of the absorbing species, as evidenced with PVA, occurs. In the same way, a crosslinking of the polymer accompanied by the modification of the chemical structure of the matrix is observed. Meanwhile, the photransformation of the host depends on its chemical structure and therefore photoproducts formed in agar are different from those observed in PVA.

Agar was *a priori* suspected to exhibit a bad photochemical stability due to the presence of tertiary carbon atom in $\alpha$ position to ether bonds. Our results show that radicals involved in the photoredox process are no able to initiate

the photodegradation of the matrix that is to say the fixation of oxygen along the polymeric chains. The stability can be attributed to the impermeability of agar towards oxygen diffusion.

Thus, the recording of real time holograms with high diffraction efficiency and the excellent photochemical stability of the host matrix allow considering dichromated agar as a natural photosensitive material.

## Acknowledgments

Drs. G. Bertrand and P.-O. Bussière are gratefully thanked for their help in performing the Knoop hardness measurements.

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