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SENSITIVITY ENHANCEMENT IN PANCHROMATIC PHOTOPOLYMERS FOR HOLOGRAPHY USING A MIXTURE OF VISIBLE-LIGHT PHOTOINITIATORS

A. Fimia, F. Mateos

Laboratorio de Optica, Departamento Interuniversitario de Optica.
Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain.

A. Beléndez

Departamento de Ingeniería de Sistemas y Comunicaciones.
Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain.

R. Sastre

Instituto de Polímeros, C.S.I.C., Juan de la Cierva, 3, 28006 Madrid, Spain.

F. Amat-Guerri

Instituto de Química, C.S.I.C., Juan de la Cierva, 3, 28006 Madrid, Spain.

ABSTRACT

Photopolymers usually present lower energetic sensitivity, and to narrower wavelength range, than other more conventional recording materials for Holography such as dichromated gelatins. We have previously overcome some of these disadvantages using a mixture of visible light photoinitiators. In present communication we describe a new aqueous photopolymer containing the monomers , methylenbisacrylamide and zinc acrylate, the initiators 4,5-diiodosuccinylfluorescein (2ISF) and Methylene Blue (MB), and the coinitiator sodium p-toluensulfinate. This formulation exhibits a dramatic enhancement of the energetic sensitivity upon radiation with 514 or 633 nm light (Ar or He-Ne laser respectively), with regard to the same mixture but with only one dye, reaching maximum diffraction efficiencies of 15-20 % with 15-60 mJ cm⁻². This enhancement is explained trough a more efficient photogeneration of initiator radicals by the ground-state formation of on ion-pair complex between cationic (MB) and anionic (2ISF) chromophoros, the proximity of which must favor electron transfer between groups. This must compensate the observed absorbance decrease at 514 nm, with regard to the absorbance of 2ISF alone in the same medium (maximum absorption at 490 nm). A clear absorbance increase at 633 nm, with regard to the absorbance of MB alone (maximum absorption at 660 nm), must also favor the photopolymerization.

1.- INTRODUCTION

Photopolymers are attractive options to other more conventional recording materials for Holography, especially for the obtention of holographic optical elements¹ and interconnection systems,² as well as for real-time holographic interferometry,³ because they can reach high diffraction efficiencies and high signal to noise ratios.⁴ However, if compared with dichromated gelatins, photopolymers show lower energetic sensitivity, with an inhibition time which retards their recording response. Moreover, the wavelength ranges at which they are sensible are usually narrow¹ and their chemical compositions directly determine the highest index modulations which can be achieved and, therefore, the values of the maximum diffraction efficiencies. Recently. we have

overcome some these disadvantages using a mixture of photoinitiators sensible to the visible light, and eliminating the inhibition time by pre-exposition of the material.⁵ In this way we have obtained panchromatic photopolymers with high energetic sensitivities, if compared with the current materiales available nowadays. As a continuation of these works, in the present paper we describe a new photopolymer based on 4,5-diiodosuccinylfluorescein, a dye already studied by our group.⁶ In the presence of Methylene Blue. The photopolymer exhibits an even more dramatic enhancement of the energetic sensitivity upon visible-light irradiation.

2.-EXPERIMENTAL

4,5-Diiodosuccinylfluorescein (2ISF) was obtained by iodination of succinylfluorescein, as described.⁷ Visible spectrum of the ionized form, λ_{max} (nm) (% ϵ , $\text{M}^{-1}\cdot\text{cm}^{-1}$): in N,N-dimethylformamide, 536(64600) and 536(42500); in methanol-pH 9 buffer 1:1 v/v, 514(53700); in the photopolymer system 514(42400). Methylene Blue (MB) was a commercial sample, used without further purification. The photopolymer consists in an aqueous solution of three monomers (acrylamide (7 M), bisacrylamide (0.7 M) and zinc acrylate (1 M)), the dyes 2ISF and MB (1:1 molar ratio) and the coinitiators sodium p-toluenesulfonate, pTS-Na ($1.7 \cdot 10^{-2}$ M), molar ratio pTS-Na/2ISF 50:1. This solution, with 70% transmittance at 514 nm, was placed between two common-glass plates with separators ($45 \pm 5 \mu\text{m}$), and analyzed by constructing holographic gratings (exposed area 5 cm^2), using symmetrical geometry in order to avoid the inclination of the Bragg planes due to possible non-uniformities in photopolymer thickness variations during the photochemical process. A spatial frequency of 950 lines/mm, when irradiating with 633 nm light (He-Ne laser), or of 1170 lines/mm, when irradiating with 514 nm light (Ar^+ laser) was used. The diffraction efficiencies of the gratings were real-time measured in an experimental set-up previously described,⁸ using the former 514-nm and 633-nm lights.

3.-RESULTS AND DISCUSSION

The dye 2ISF was chosen as the basis of the present photoinitiator system because of its high absorption, either in ionized or in quinonoid form, at 514 nm, the wavelength of the emission line of the Ar^+ laser. In the photopolymer system, this dye must adopt mainly the quinonoid form, with an absorption spectrum with a maximum flanked by two bad-defined shoulders (Fig. 1), as observed in other xanthene dyes in neutral media.⁹

However, the high transmission value measured at 514 nm points to the presence of an important proportion of the ionized form of 2ISF, non distinguishable in the absorption spectrum of the solution. The presence of colorless xanthidric and ethylenic forms, already observed in the parent non-halogenated dye succinylfluorescein,¹⁰ can't be disregarded.

The changes in diffraction efficiencies of holographic gratings (spatial frequency 1170 lines/mm) with the exposition to 514 nm light, in photopolymers containing 2ISF or the 1:1 mixture 2ISF/MB is shown in Fig. 2.

Figure. 1. Absorption spectra of solutions of 2ISF ($\lambda_{\max}$ 419 nm), and of the 1:1 mixture 2ISF/MB ($\lambda_{\max}$ 663 nm) in the photopolymer system diluted with water (solid lines).

Figure. 2. Comparative evaluation as holographic recording systems, under irradiation with 514 nm light and 633 nm.

As it can be seen, both systems reached a maximum diffraction efficiency close to 20%, whilst the necessary energy for reaching this value dropped from ca. 1000 mJ.cm⁻² to ca. 66 mJ.cm⁻² when MB was present. This is a consequence of the important decrease of the inhibition time in the latter system, with regard to the system with 2ISF alone. Moreover, irradiation with 633 nm light of the system with the two-dyes increases the sensitivity about four times, if compared with the irradiation using 514 nm light (Fig. 3),

or sixty times, if compared with the same system irradiated with 514 nm light, but with 2ISF alone (Fig. 2). to our knowledge, the system herein described shows sensitivity comparable to the available commercial photopolymers. Besides, this sensitivity is about ten times higher than those shown by photographic emulsions upon high exposure. However, the maximum diffraction yields which can be reached are not high.

Figure 3. Evaluation as holographic recording system of a photopolymer with the 1:1 mixture 2ISF/MB. Change of the diffraction efficiency with the recording energy (E) when irradiating with 514 nm light (circles) (1170 lines/mm, 0.44 mW/cm²). Transmittance 70% at 514 nm.

Although the interpretation of these results is still under study, it is possible to advance some hypotheses in order to justify the observed behaviour. The obtained results indicate that the system with 2ISF/MB gives rise, upon irradiation, to more initiation radicals, and at a higher rate, than the one with 2ISF alone. This fact must be attributed to efficient photochemical intramolecular electron transfer processes between the two dyes, yielding semioxidized and semireduced species much more reactive than each dye alone.¹¹ The sensitivity increase shown by the 2ISF/MB system upon irradiation with 633 nm light, with regard to the irradiation with 514 nm light, is a consequence of the much higher absorption of the photopolymer at 633 nm, with an absorbance ratio A_{633}/A_{514} of about 10:1, as deduced from the absorption spectra of diluted aqueous solutions, whilst the expected ratio should be about two times. This strong decrease in the absorbance of the system at 514 nm, in the zone where 2ISF absorbs, points to the formation of colorless forms, very probably with xanthidic structure, by acid-catalized [1,6] addition of water to the quinonoid group, as already observed in the parent compound succinylfluorescein in other mediums.¹⁰ The acidity would be provided by MB, a quaternary ammonium salt (chloride). A small absorbance increase at 633 nm, in the zone where MB absorbs, with regard to a comparative system with MB alone, can be the result of some deaggregation of the dye, induced by the presence of the other dye. The shape of the absorption spectrum of MB is very sensible to the dye concentration and to the presence of salts.¹² Ground-stage charge transfer between 2ISF and MB can be another process to be taken into account in

the interpretation of the differences observed between photopolymers with each dye alone that with their mixture. Absorbances changes in the contrary sense have been observed in more diluted (ca. 10^{-5} M) aqueous solutions of mixtures 2ISF/MB in molar ratios in the range 0.7–2.6. This different behavior is an indication of the complexity of the photochemical and, may be, thermal mechanisms evolved, the macroscopic experimental consequence of which is the sensitivity enhancement observed in the monomer mixture herein described.

4.-CONCLUSIONS

We have shown that the combined action of two dyes as visible photoinitiators can give rise to an enhancement of the energetic sensitivity in photopolymers. At the same time, the systems became panchromatic, i.e. sensible to more than one wavelength. The observed effect of the dye mixture, which can be correlated with the superadditivity shown by developer mixtures in photographic emulsions, can be of potential utility when recording multifunctional diffractive systems, as well as in real-time holographic interferometry with two wavelengths.

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