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Refractive index modulation in polymer film doped with diazo Meldrum's acid

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Abstract. Diazo Meldrum's acid undergoes a photoreaction induced by UV light and it is used as photosensitizer in photoresists. Upon photoreaction, a change in refractive index occurs, which makes this system interesting for volume holography. We report on the sublimation effect at room temperature and the effect of photoirradiation on the refractive index in thin films of CAB (Cellulose acetate butyrate) doped with different amount of diazo Meldrum's acid. A net modulation of the refractive index of 0.01 is achieved with 40% of doping ratio together with a reduction of the film thickness.

Keywords. Refractive index, diazo Meldrum's acid, CAB, holography, photopolymers.

1. Introduction

The modulation of the refractive index in materials is a key property for designing and manufacturing volume holographic optical elements and waveguides[1-5]. Materials where the change in refractive index is induced by a light stimulus are good candidates and photopolymers[6-7], silver halides[8], dichromated gelatins (DCGs)[9-10] or photochromic materials[11] have been known since a long time. Materials for holography can be classified according to the possible self-developing property that is the capability to induce the modulation just by the light stimulus without any chemical post-processing. This is the case of photopolymers and photochromic materials, whereas DCGs and silver halides actually require a chemical process to enhance the impressed pattern (from the latent image to the hologram). Especially for DCGs, the chemical developing leads to very large refractive index modulation thanks to the creation of microvoids[6,12]; moreover, it enables a fine tuning of this modulation. More recently, other polymeric systems have shown a change in the refractive index, which is mainly related to a material density variation induced by a photoisomerization, i.e. Photo-Fries rearrangement[13-15] . In this context, research of

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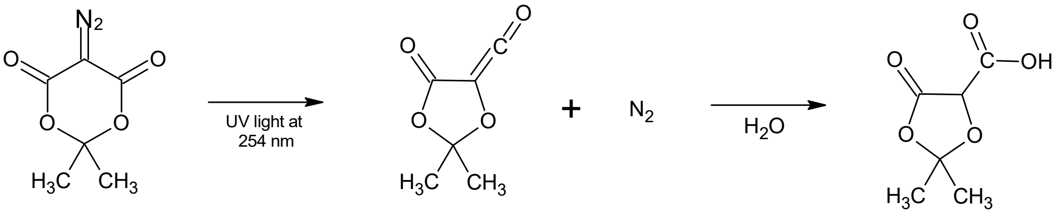
new systems and reactions that provide a change in refractive index is thus of large interest and self-developing systems that mimic the mechanism of DCGs (microvoid creation) are actually desired. Hints can be found in materials developed for deep UV lithography and in particular in diazocarbonyls[16-17]. 5-Diazo Meldrum's acid (DMA) is a sensitizer in positive photoresists and its photoreaction has been deeply studied both in solution and in polymer matrix[17-18]. The reaction mechanisms have been also detailed through fast spectroscopy supported by theoretical calculations[19-20]. Irradiation of DMA with UV light causes the loss of a nitrogen molecule (scheme 1) together with the formation of a ketene (Wolff rearrangement), which can also react with alcohol or water to provide an ester or a carboxylic acid. Actually, DMA follows different reaction paths depending on the illumination condition and the local environment[19].



Scheme 1. Basic photoreaction of DMA upon irradiation at 254 nm and in the presence of water.

As the light-triggered loss of N_2 groups is expected to bring to a drop in the molecular polarizability of the system, in this paper, we study the induced modulation of the refractive index by UV-irradiation in CAB (Cellulose acetate butyrate) films doped with DMA. We demonstrate that sublimation of DMA occurs at room temperature thus turning into a small change in the refractive index. A much larger modulation is achieved by UV illumination, where the 5-member ring carboxylic acid derivative of the DMA is obtained (scheme 1).

The potential applications of this system are in the manufacturing of volume phase patterns as "ready to use" complex optical waveguides by means of a standard UV direct writing approach. Moreover, it can be the baseline for a new class of materials for making dispersing elements (volume phase holographic gratings), holographic filters and computer generated holograms (CGHs).

2. Methods and Materials

2.1 Film preparation and light exposure

Cellulose Acetate Butyrate (Eastman CAB-531-1) was dissolved in chloroform with a concentration of 4% w/v; DMA was added to the solution with a concentration of 10, 20 and 40% w/w in respect to CAB. The solutions were spin coated on different substrates (silicon, fused silica, BaF_2) depending on the target characterization technique with a rotation speed of 8000 rpm using a Polos 300 spin coater. The thickness of the films was in the range 200–300 nm. To induce the photoreaction, the films were exposed to UV light at 254 nm (11.8 mW/cm^2 measured with a photodiode Thorlabs S130VC placed the same position of the sample) by means of G4T5 germicidal UV lamp.

2.2 UV-vis and infrared spectroscopy

The UV-vis spectra were collected using a Jasco V570 spectrometer. The substrate for the thin films was quartz in order to make possible acquisition down to 200 nm. The absorbances were corrected of the reflection losses, by subtracting the absorbance at 400 nm where no absorption takes place.

The IR spectra of polymeric film deposited on BaF_2 substrates were recorded using a FT-IR Nicolet Nexus equipped with a DTGS detector (32 scan, 4 cm^{-1} of resolution). The IR spectra were visualized and analysed using the software Thermo Scientific Omnic^{TM} 7.1. As in the case of UV-vis spectra, peak absorbances were determined taking into account the baseline in the spectra.

2.3 Refractive index and thickness measurement

The two parameters, namely the refractive index (n) and the thickness, have been retrieved from spectral reflectance measurements recorded by a Filmetrics F20-EXT in the range 400–1700 nm. Thin films were deposited on Si substrates in order to have a large refractive index mismatch that turned into a large reflectance modulation. A fitting procedure, implemented in Matlab®, then was applied to the reflectance spectra, using a four-term Sellmeier model[21] (equation 1) for the refractive index of the polymer film as function of the wavelength:

$$n^2(\lambda) = 1 + \frac{B_1\lambda^2}{\lambda^2 - C_1} + \frac{B_2\lambda^2}{\lambda^2 - C_2} \quad (1)$$

where λ is the wavelength and $B_{1,2}$, $C_{1,2}$ are the fitted parameters. In particular, the C_i parameters represent the resonance frequencies of the Lorentz's oscillators used to modelling the system. Such model describes in a good fashion the trend of the refractive index for dielectric materials not only in the visible, but also in the NIR spectral region.

From the Sellmeier model, the refractive index at static electric field was calculated as $(1+B_1+B_2)^{0.5}$.

3. Results and Discussion

To highlight the effect on the refractive index triggered by the photoisomerization of DMA, thin films of CAB were deposited by spin coating using the procedure reported in section 2.1. CAB is a thermoplastic cellulose ester, which is soluble in many solvents and it is used as polymer matrix in several photopolymers formulations[22,23]. The polymer is characterized by a wide range of transparency down to 240 nm, thus not shielding the UV absorption of DMA, which is peaked at 250 nm (see figure 1 on the left). The IR spectrum was also used to monitor the proceeding of the light- induced photoisomerization of DMA, since it shows some separated bands from those of the CAB matrix. Specifically, in the CAB+DMA FTIR spectrum reported in figure 1, signals characteristic of the DMA are: i) the band at 2174 cm^{-1} due to the stretching of the $-N_2$ group; ii) the C=O stretching at 1723 cm^{-1} that is partially overlapped with the C=O stretching of CAB; iii) the band at 1335 cm^{-1} due to the C-N stretching[24].

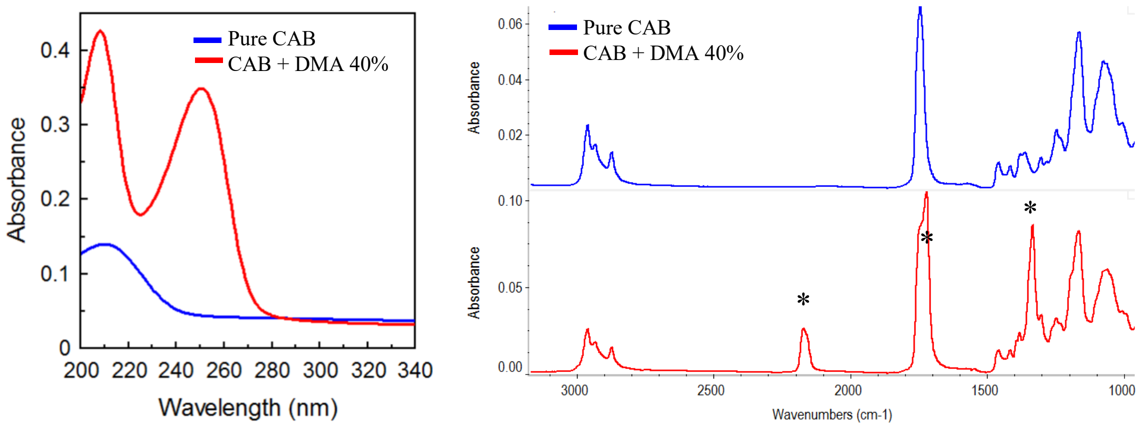


Figure 1. UV and IR spectra of pure CAB (blue line) and CAB+DMA 40% (red line). The stars identify the significant DMA bands.

Among these, the band at 2174 cm^{-1} is the most interesting one, since it is isolated and highly specific of the diazo group.

3.1 Spectroscopic behaviour of CAB+DMA

To assess the loss of DMA in CAB matrix before irradiation, we monitored the evolution of the peak absorbance at 250 nm at room temperature as function of time for different concentrations (figure 2). Such characterization, was carried out since the sublimation of the DMA from a polymer matrix has been already reported in the literature [16-17], but without any quantitative analysis.

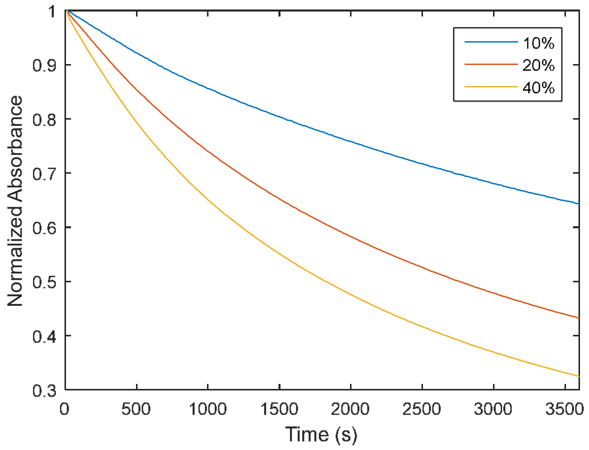


Figure 2. Plot of the normalized absorbance measured at 250 nm, for CAB films doped with 10, 20, 40% of DMA as function of time at room temperature.

The normalized absorbance significantly decreases with time, right after the sample preparation, and tends to reach a plateau value indicating that sublimation occurs at all the tested concentrations. The rate of decrease is proportional to the initial concentration and we notice that storage times of the order of hours are required to approach the plateau value. The faster kinetics for higher DMA concentration is unfavourable, as heavy DMA doping is required to maximize the refractive index change by photoexposure.

Since the UV-vis spectrum does not show any change other than the decrease of absorbance, IR spectra at different elapsed time has been collected. In figure 3, the evolution of the band at 2174 cm^{-1} is reported for the sample doped with 40% of DMA up to three hours.

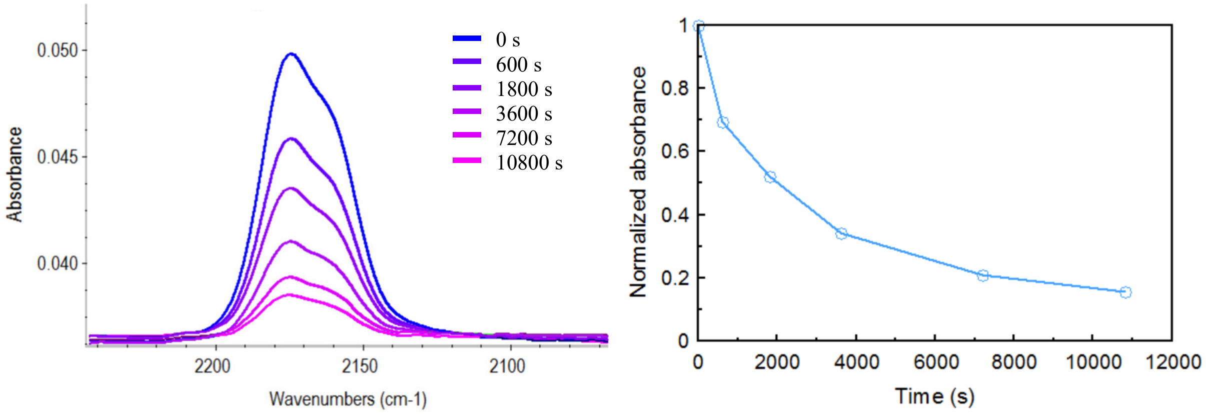


Figure 3. On the left: evolution of the band at 2174 cm^{-1} as function of the stored time at room temperature. On the right: the normalized absorbance of the same band.

Moreover, no new band grows up in time, thus confirming that sublimation of the doping molecule only occurs without a degradation or a chemical transformation.

According to these results, the UV exposure to address a significant refractive index change has to take into account the sublimation, namely it has to be fast enough to minimize the loss of material. Thin films of CAB with 40% of DMA were prepared and immediately exposed to different doses of UV light at 254 nm; the evolution of the signals characteristic of DMA was monitored by both UV-vis absorption spectroscopy and FT-IR spectroscopy.

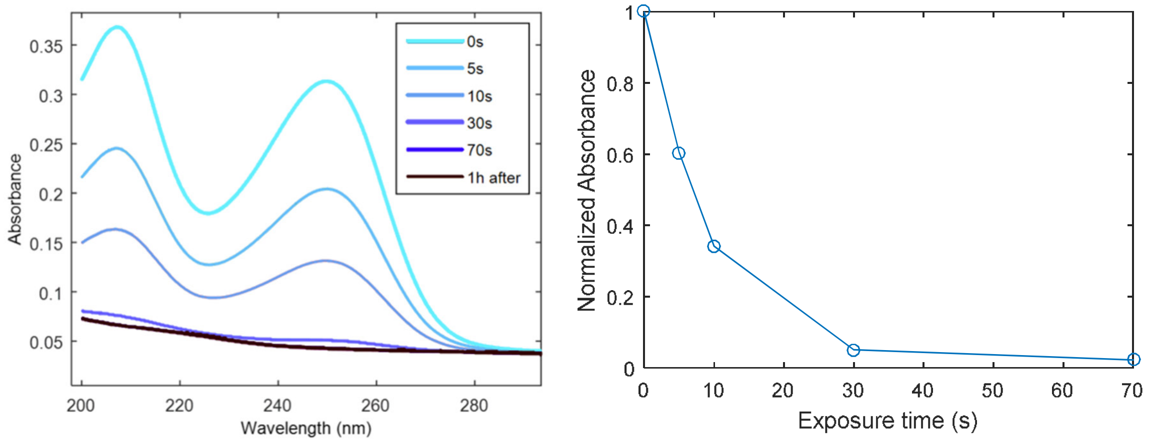


Figure 4. UV spectra of CAB+DMA at different exposure times at 254 nm. On the right, the evolution of the normalized absorbance at 250 nm.

The intensity of the band at 250 nm quickly decreases in intensity and it almost disappears in 30 seconds, as reported in figure 4, thus indicating that no residual DMA remains upon photoexposure. This result differs from the thermal evolution (i.e. sublimation) where an equilibrium DMA concentration was reached.

The same behaviour was highlighted with IR spectroscopy, as shown by the decrease in intensity of the band at 2174 cm^{-1}, which is reported in figure 5 as a representative example. The normalized absorbance of this band strongly decreases within 30 seconds and completely disappears in 70 seconds in accordance to the UV spectroscopy results. The bands at 1723 cm^{-1}, and at 1335 cm^{-1} show similar trends.

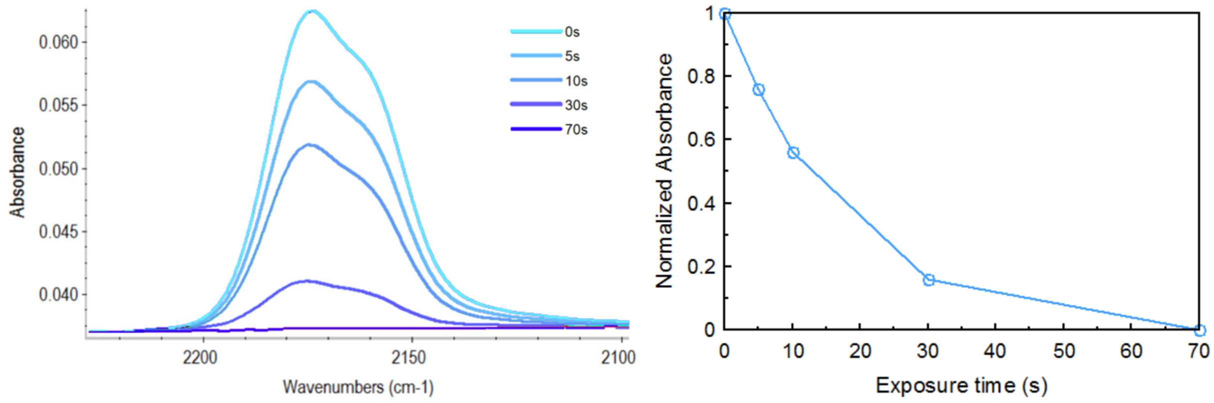


Figure 5. On the left: evolution of the IR band at 2174 cm^{-1} for different exposure times at 254 nm. On the right: the evolution of the normalized absorbance at 250 nm.

Interestingly, looking at the differential IR spectra (figure 6 on the left), two new bands appear at 1802 cm^{-1} and at 1766 cm^{-1} that are consistent with the formation of the carboxyl derivative, which is the main product when the DMA is photoexcited at 254 nm in presence of water (in the present case dissolved in the CAB matrix). Another evidence of such reaction is the growth of –OH stretching band at about 3200 cm^{-1}(inset in figure 6 on the left). A similar behaviour, with the formation of a –COOH group, was highlighted in PMMA films doped with DMA [17]. The important effect is that the main product formed by photoexcitation is not volatile nor does not sublimate, since the IR spectrum collected one hour later the last UV exposure remains unchanged (figure 6 on the right).

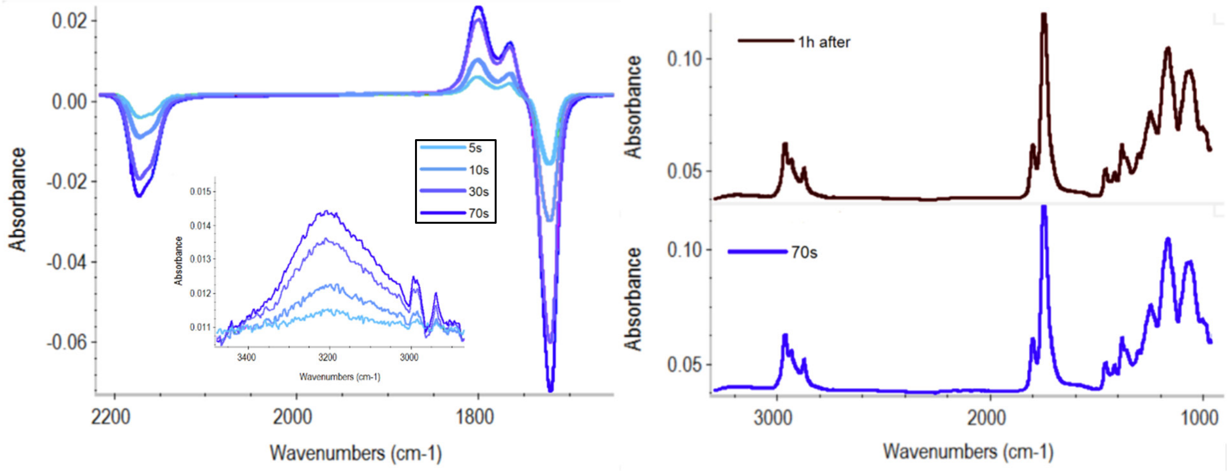


Figure 6. On the left: differential IR spectra at different UV exposure times. On the right: the IR spectrum after 70 s of UV exposure and then after one hour at room temperature.

Such evidence is of great relevance since it means that UV-exposure leads to a stable system, which is mandatory when a pattern of refractive index modulation has to be impressed.

3.2 Refractive index modulation

A modulation of the refractive index is expected for both storage at room temperature and UV exposure of the CAB films, with different effects since the DMA undergoes specific evolutions in the two cases. The change in the refractive index can be the consequence of: i) a change in the polarizability of the DMA before and after the reaction; ii) a change in the DMA concentration because of the sublimation; iii) a change in the density of the material. In order to measure the refractive index, the spectral reflectance of thin DMA+CAB films on Si substrates was measured in the range 400–1700 nm. Applying a fitting procedure based on the Sellmeier model, both the dispersion curve of the refractive index and the film thickness were evaluated. As important parameters, we selected the refractive index at static electric field (see paragraph 2.3 for the details) and the film thickness. In figure 7, the modulation of the refractive index at static electric field (Δn) and the film thickness (d) are shown for a sample CAB+DMA 40% stored at room temperature in the dark.

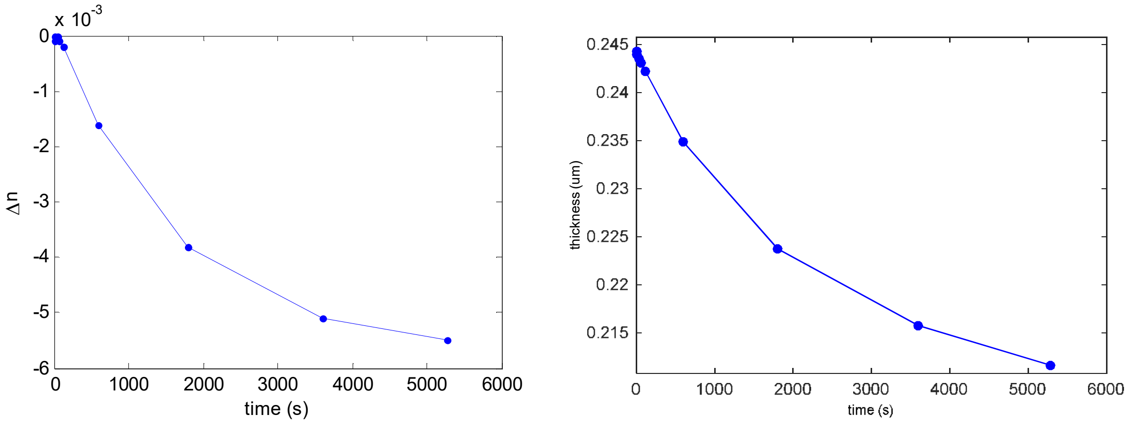


Figure 7. On the left: refractive index modulation as function of time at room temperature in the dark; on the right: film thickness evolution as function of the elapsed time.

DMA sublimation turns into a loss of polarizable molecules from the solid medium, with a consequent decrease of the refractive index during time (negative Δn). Moreover, the simultaneous film thickness decrease (-13.4%) means that the CAB macromolecular chains recover the free volume while DMA species are removed from the polymer matrix. Accordingly, material density does not change or even increases. These two effects, namely polarizability and thickness, here play opposite roles on the overall refractive index modulation, which reaches a value of $5.5\text{x}10^{-3}$.

The same analysis has been performed on photoexposed samples, and the plots of Δn and d as function of the UV dose (proportional to the exposure time) are reported in figure 8.

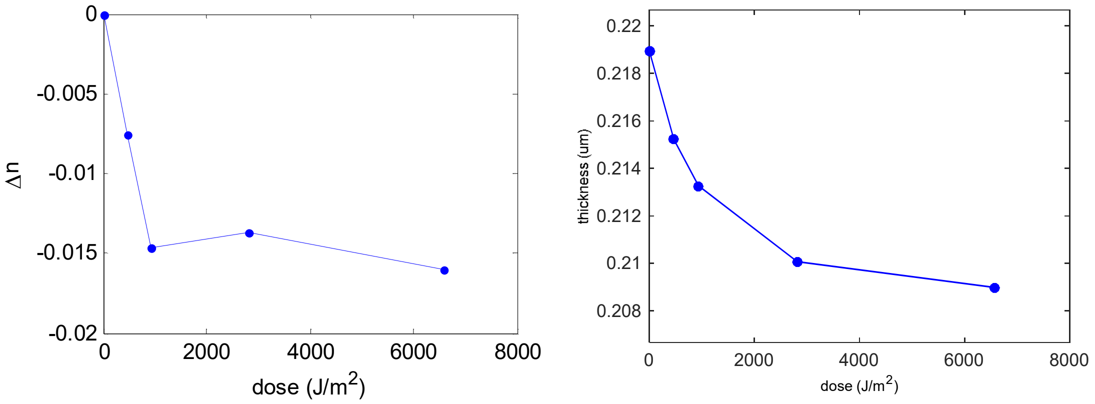


Figure 8. On the left: refractive index modulation as function of the UV dose; on the right: film thickness as function of UV dose.

The Δn becomes more and more negative with the UV dose, meaning that a decrease in the refractive index accompanies the photoreaction. This finding can be explained considering the chemical structure of the main photo-product, which does not contain the highly polarizable -N_2 group. Even for the photo-exposure, a shrinkage of the film thickness (-4.6%) takes place although it is smaller than in the previous case. This result is consistent with the fact that, by UV-irradiation DMA molecules are not completely removed from the polymer matrix, but the photo-products occupy a certain volume, thus likely limiting the thickness reduction. Overall, the strong change in polarizability between DMA and the resulting photo-product (the carboxylic derivative in scheme 1) together with the minor shrinkage result into a larger refractive index modulation, of the order of 0.015. This value is three fold than the value due to the sublimation and it is large enough for making efficient phase holographic elements.

It is worth to compare the Δn of CAB+DMA system with the Δn of other materials for phase holography. The Δn is smaller than in the case of DCGs, which can reach values of 0.15 and it is the material with largest values. The difference can arise from the fact, that in CAB doped films, the change in modulation is mainly due to the loose of a highly polarizable N_2 molecule, but the CAB matrix partially fills the free volume. In the DCG, the microvoids that are created in the material volume are due to a crosslinking process followed by a chemical treatment of swelling and drying. Therefore, the gelatins macromolecules cannot relax filling the microvoids and this turns into a large drop in the refractive index and a large value of the modulation. The advantage here consists in the fact that the CAB+DMA system is self-developing and a possible improvement could come from the modification of the polymer matrix in terms of stiffness to reduce the relaxation during the reaction. If we compare the results of Δn with other photosensitive systems sensitive to UV light as in the case of Photo-Fries systems, we found slightly smaller values (they can reach 0.05), mainly because of a difference in the concentration of the active species. The Photo-Fries systems reported in the literature are polymers with the photoactive species in the polymer chain, so the concentration is large. In our case, the DMA is dispersed in the polymer matrix and the concentration cannot be increased at will. Moreover, Photo-Fries based materials become usually more and more opaque to the writing UV wavelength, preventing the conversion in thick films. In the system here studied, it occurs exactly the opposite, making easier the writing of phase pattern in thick films. An improvement of our system in this direction could be the synthesis of polymers bearing the DMA as side chain. Besides, with this approach will be avoided the sublimation of the compound, improving the stability of the system.

4. **Conclusions**

The behaviour of CAB film doped with DMA has been evaluated in terms of refractive index modulation in order to understand whether this material can be effectively used for volume phase holograms (e. g. diffraction gratings). Refractive index change was generated both by sublimation of DMA, which occurs spontaneously at room temperature, or by exposure to UV light at 254 nm. As regard the polarizability, in the former case the polymer matrix was depleted by the polarizable DMA molecules, whereas in the latter the photo-products (i.e. a carboxylic acid derivative without any N_2 group) that remain embedded in the CAB, shows a lower polarizability lower than the starting DMA species.

In both cases, removal of molecular species form the polymer matrix turned into a reduction of the film thickness, which was more significant in case of sublimation. In terms of final Δn, this shrinkage opposed to the effect due to polarizabilty. It followed that a limited reduction of the refractive index of about 0.006 after three hours resulted in the case of sublimation.

Upon photoirradiation at 254 nm, a much larger drop in the refractive index was achieved (0.015), as generated by the significant change in polarizability combined to a small shrinkage of the film thickness.

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