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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.

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 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 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].

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

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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 was quartz in order to make possible acquisition down to 200 nm. The absorbances were corrected of the reflection losses, by subtracting the absorbance value 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™ 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, were 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®, 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 model 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 Fig. 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 Fig. 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].

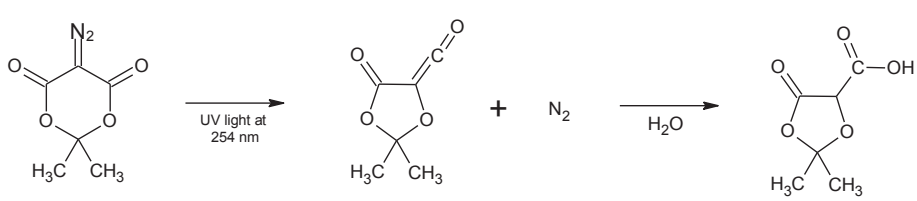
Among these, the band at 2174 cm^{-1} is the most interesting one, since it is isolated and highly specific of the diazo group.

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 (Fig. 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.

The normalized absorbance significantly decreases with time, right after the sample preparation, and tends to reach a plateau value with storage times of the order of hours. Sublimation occurs at all the tested concentrations with a rate of decrease on the left, proportional to the initial concentration. 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 Fig. 3, the evolution of the band at 2174 cm^{-1} is reported for the sample doped with 40% of DMA up to



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