Optical and holographic characteristics of photopolymer layers♣

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The present work studies the optical and holographic characteristics of acrylamide-based photopolymer layers. The refractive index change of a liquid acrylamide photopolymer due to exposure at 532 nm is obtained for the first time, using a critical angle laser micro-refractometer. The 30 μm thick solid photopolymer films are prepared by casting on glass substrates. Bragg holographic gratings with spatial frequencies of 710 mm^{-1}, 1050 mm^{-1} and 1600 mm^{-1} are recorded using a diode laser operating at 532 nm wavelength. We investigate the dependence of the diffraction efficiency on the exposure energy. The obtained results are compared with the Stetson holographic recording method, where two gratings are simultaneously recorded in the same location with spatial frequencies of 2020 mm^{-1} and 3670 mm^{-1}, using a totally reflected reference wave from the air-photopolymer interface. Despite the fact that in the latter method the two gratings share the same dynamic range, higher diffraction efficiencies are observed.

1. Introduction

Photopolymers are applied in holographic sensors [1, 2], holographic data storage [3-5], fabrication of holographic optical elements [6], security holograms [7], electro-optical switchable devices [8], and also some non-imaging applications such as adhesives, coatings and inks [9]. Since the lasers and the optical systems for work in the UV are expensive, the majority of photopolymers are designed to respond to visible light. The basic formulation of the dry photopolymer system contains a photoinitiator and a monomer dispersed in a binder matrix. In the investigated acrylamide-based photopolymer system, photoinitiation is a two step process. Upon illumination of the photopolymer with light of appropriate wavelength, the sensitizing dye absorbs a photon and reacts with an electron donor to produce free radicals (initiation step). These initiate polymerization where the light was absorbed. Chain propagation or termination follows the initiation. Currently accepted models describe the recorded pattern formation as a result of changes in the density and the molecular polarizability, which accompany the polymerization. The models [10-12] show that the key factor controlling the dynamics and final properties of the recorded hologram (refractive index space profile and modulation) is proportional to the ratio of the polymerization and monomer diffusion rates. Both parameters are strongly influenced by the nature of the photopolymer system, and having independent information about the diffusion and polymerization rates is important for optimization of the photopolymer system. We have previously characterized the monomer and short polymer chain diffusion rates at the initial stage of holographic recording in acrylamide base-photopolymers [13] as well as the polymerization rate during homogeneous illumination by Raman spectroscopy [14]. In the present investigation, we focus our attention on the description of the polymerization rate by determination of the photoinduced changes in the surface refractive index during homogeneous illumination and polymerization. The surface refractive index is measured at 532 nm wavelength by a laser refractometer. The properties of the holographic recording are also characterised and compared using two different geometries.

2. Experimental details

2.1 Sample preparation

A stock unsensitised photopolymer solution is prepared by mixing 2.4 g of acrylamide, 0.75 g of N,N'methylene bisacrylamide, 4.5 ml of triethanolamine and 52.5 ml of (10 wt.% PVA stock solution). Erythrosine B stock solution of 0.11 wt.% concentration is prepared by adding 0.11 g of dye to 100 ml distilled water. In order to prepare sensitised layers, 5.0 ml of photopolymer stock solution are mixed with 0.07 and 1.0 ml of dye stock solution resulting in dye concentrations of 0.7 and 1 wt.% respectively. For surface refractive index measurements, liquid layers are prepared by depositing 0.03 ml on a glass slide. The solid layers are obtained by casting 0.3 ml on microscopic slides and drying for 24 hours in the dark.

2.2 Optical measurements

The transmission spectra of the solid samples are measured with 0.01 % experimental uncertainty in the 400 nm - 800 nm spectral region, by a Cary 5E spectrophotometer. The refractive index (RI) is measured with a laser micro-refractometer at 532 nm, i.e. in the absorption band. The method was earlier described in detail in [15, 16]. In brief, the determination of the critical angle is carried out with the help of a metal grating allowing observation if total internal reflection at the prism/photopolymer layer interface occurs. The photopolymer layer is located between a prism of high refractive index ($n_p > 1.5$) and the grating. At lower angles of incidence, the laser beam is transmitted through the sample and the grating, and a diffraction pattern is observed. At a critical angle of incidence, total internal reflection occurs, the beam does not pass to the grating and the diffraction pattern disappears. The experimental uncertainty depends mainly on the accuracy of the goniometer used - a "Microcontrole" rotary stage with 1 arcmin resolution. With this experimental refractometer, the RI is measured with an experimental uncertainty of ± 0.0002 for liquid samples, and of ± 0.0005 for the solid ones.

2.3 Holographic recording set-up

As illustrated in Fig. 1, a symmetrical two-beam interference set-up is used for holographic grating recording in the Bragg regime with three different angles: $2\theta = 21.7°$, $32.24°$ and $50.33°$ between the recording beams of light. The corresponding spatial frequencies are 710 mm^{-1}, 1050 mm^{-1}, and 1600 mm^{-1}. A low-intensity He-Ne laser is employed as a read-out beam to monitor the buildup dynamics of the grating during the holographic recording.
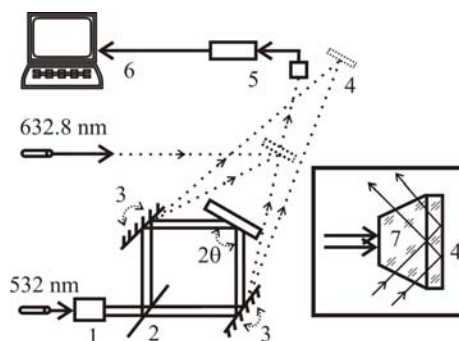

Fig. 1. Holographic setup: 1- beam expander; 2- beam splitter; 3-mirrors; 4-photopolymer; 5-powermeter; 6-computer; 7-glass prism.

The total laser beams' intensity is 10mW/cm^2. Two high spatial frequency gratings are simultaneously recorded in the Stetson regime, using the holographic setup [17] presented in the inset of Fig.1. The reference beam is totally reflected from the photopolymer - air interface at the 65° incidence angle. The object beam is incident normally on the photopolymer. Transmission and reflection gratings are simultaneously recorded with spatial frequencies of 2020 mm^{-1} and 3670 mm^{-1}, respectively.

3. Results and discussion

The transmission spectra for 0.7 wt% and 1.0 wt% dye concentration are presented in Fig. 2.

The photopolymer is optimised for recording at 532 nm and the sensitizer (Ertythrosine B) has a maximum absorption at 535 nm.

The results of RI measurements of liquid photopolymer layers characterized by different dye concentrations after exposure at 532 nm are presented in Fig. 3. As expected, the RI increases after illumination.

Starting from RI = 1.3632 ± 0.0002, in both cases the RI increases immediately and achieves different saturated values at different exposure levels, depending on the dye concentration. Despite the 0.3 wt% difference in dye concentration, the saturated RI values for 1 wt% are about 0.001 higher, revealing that this dye concentration provides more efficient polymerization and a larger RI change.
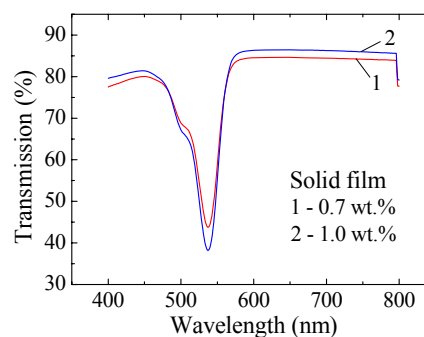

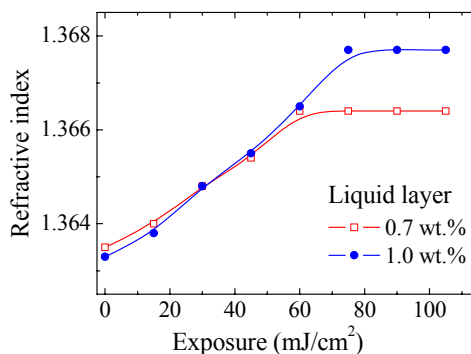Fig. 2. Transmission spectra dependence on the dye concentration.

Fig. 3. Evolution of the refractive index of the liquid layers, versus exposure.

Quite different is the RI dependence on exposure for the solid films, illustrated in Fig. 4.
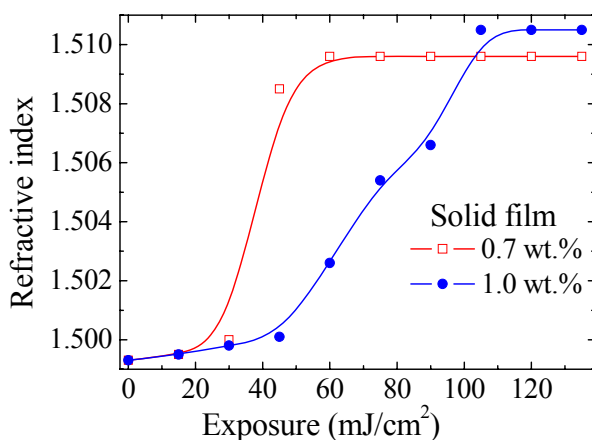

Fig. 4. Evolution of the solid films' refractive index versus exposure.

For the dye concentration of 0.7 wt%, a threshold exposure of 30 mJ/cm² is observed, rising to 45 mJ/cm² for 1 wt%. The RI saturation exposure of 60 mJ/cm² for 0.7 wt% is the same for the film and the liquid layer. The results of the RI investigations are summarized in Table1. The refractive index difference is:

$$\Delta RI = RI_{E=0} - RI_{E=E_{saturation}} \qquad (1)$$

Table 1. Summarized results from the refractive index measurements.

Sample	C (wt.%)	$E_{saturation}$ (mJ/cm²)	Saturated RI, ±2·10⁻⁴ (±5·10⁻⁴)*	Δ RI
liquid layer	0.7	60	1.3664	0.003
	1	75	1.3677	0.004
Solid film	0.7	60	1.5096*	0.010
	1	105	1.5105*	0.011

The observed differences in the RI dependence on the exposure and dye concentration for liquid formulations and solid films can be explained having in mind that the penetration depth in the total internal reflection case is about 1 μm [18].
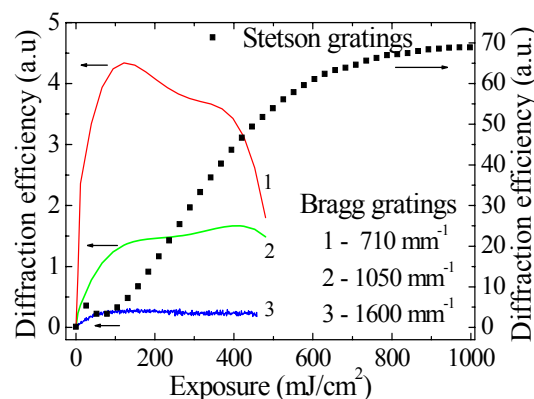

Fig. 5. Diffraction efficiency dependence on exposure.

Near the boundary between a glass prism and a liquid phase, the surface tension is smaller, compared with that at the glass substrate – film boundary. In this case the RI change due to photopolymerization is observable almost immediately, in less than 0.1 sec. On the other hand, near the solid film surface, this process is delayed by the higher surface tension. The difference between the saturated RI values of the solid film and liquid layers for the two different concentrations is similar –0.143 ± 0.001, and in this concentration range does not depend on the dye concentration.

The diffraction efficiency (DE) dependence on the exposure is shown in Fig. 5. It is interesting to note, that the DE for the transmission Bragg gratings is much lower compared with the two gratings DE, simultaneously recorded by Stetson's method in the same location.

In order to explain this effect, two important facts should be taken into account: 1. The two Stetson gratings are of different types (reflection and transmission) and their angles of reconstruction and diffraction coincide. 2. The dynamic range of the RI modulation (Δn) is large enough to be shared and to achieve a high DE.

From Kogelnik's coupled wave theory [19], for 100 % DE one needs a RI modulation, according the following relation:

$$\Delta n = \frac{\lambda \cos \theta}{2d} \qquad (2)$$

For $\theta = 30^\circ$, $\lambda = 532$ nm and $d = 30$ μm, the needed RI modulation is $\Delta n = 0.0077$.

Table 1 illustrates that the RI change is enough to ensure simultaneous recording of the two gratings with a relatively high DE.

4. Conclusions

In summary, the refractive index changes upon illumination of liquid and solid photopolymer layers at 532 nm are measured with a laser microrefractometer.

In solid films, this change is approximately twice that in liquid layers. The investigated photopolymer can be used for holographic recording not only as a solid film, but also as a liquid recording medium. This could prove useful in the development of photopolymerisable nanocomposites, where high permeability is required to achieve redistribution of nanosized dopants and a consequent improvement of the recording dynamic range. This is very important for multiple holographic data recording. Another interesting application is in colour holographic recording with blue, green and red lasers, after appropriate spectral sensitization.

References

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