Refractive-index patterns in doped PMMA films, recorded with a HeNe laser

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The red sensitive photoinitiator system eosin–methyleneblue was introduced into thin PMMA films (10–20 μm). 2-Hydroxy-2-methyl-1-phenylpropan-1-one (Darocur 1173 (Merck)) was used as an intermediate solvent. The photopolymerizable monomer was styrene. Refractive index patterns were recorded with HeNe laser light. The thermal stability of the photoinitiator system and the measured refractive index profiles are discussed. Developed and fixed refractive index patterns could be obtained by an annealing procedure with Δn up to 0.006.

(Keywords: optical waveguiding; light-induced refractive index changes; red sensitive photoinitiator; refractive index profiles)

INTRODUCTION

Usually refractive index patterns in thin films of photopolymers are recorded via u.v. lithography. In principle the optical sensitivity of a photopolymeric system may be shifted by selecting the photoinitiator. The availability of HeNe lasers (632.8 nm) gives a photoinitiator system which is sensitive in the red spectral region which is quite attractive. There are successful studies[1,2] using methyleneblue as a photoinitiator in aqueous systems. The purpose of this paper is to report the results obtained transferring this photoinitiator alone and together with eosin into the PMMA matrix. Furthermore, the thermal stability of this photopolymeric system and the formation of refractive index profiles during exposure and subsequent annealing treatment are discussed.

EXPERIMENTAL

As a red sensitive photoinitiator the dye eosin–methyleneblue was used. The dye was dissolved in 2-hydroxy-2-methyl-1-phenylpropan-1-one (Darocur 1173), supplied by Merck[3]. This solution was mixed with a solution of PMMA in (chlorobenzene + styrene 80/20). From this final mixture photosensitive polymeric films were fabricated by a deposition technique. PMMA and styrene were purified as described in a previous paper[4]. The composition of the photopolymeric system was: PMMA, 30 wt%, Darocur 1173 intermediate solvent, 69.75 wt%, eosin–methylene blue photoinitiator, 0.25 wt%, and a residual amount of styrene monomer.

Styrene was chosen as the monomer because of its higher boiling point and higher refractive index compared with methylmethacrylate (MMA). The amount of residual monomer still present in an 'as dried' film may be assumed to be about 15% according to an earlier study[4]. The concentration of Darocur was chosen to be high for the following two reasons:

(1) The photoinitiator concentration should remain unchanged as long as possible without crystallization during the exposure or annealing procedure.

(2) Darocur 1173 is known to undergo a large change in refractive index during u.v. exposure. An induced reaction by the photochemically activated eosin or methyleneblue dyes should be detectable for high concentrations[5].

The polymer films were either deposited on u.v. glass substrates or on one surface of a regular 60° prism made of Flint gass with $n_p = 1.62$. Absorption measurements were carried out with a Cary 17D spectrometer. The mode spectra were measured using the polymer film as a leaky waveguide coated directly on the input prism[6]. HeNe lasers were used for recording the mode spectra and for exposure. Measurements were performed with low energies as compared with the exposures.

The anisotropy of the refractive index was below the accuracy of the measurements, and thus we restricted this study to the TE modes.

RESULTS AND DISCUSSION

Photoinitiator system

In *Figure 1* the absorption spectrum of a 10 μm thick polymer film doped with eosin–methyleneblue is plotted The absorption maximum at 660 nm corresponds to methyleneblue and the peak at 530 nm to eosin. Curve A in *Figure 1* represents the unexposed film, while curves B and C show the absorption changes after 15 min and 45 min exposure to HeNe laser light, respectively. Irradiation power density was 0.8 mW cm^{-2}. The surprising fact is that both absorption peaks decrease simultaneously. Measurements of films doped with methyleneblue alone show a decrease of the absorption peak around 660 nm upon exposure. The photochemically activated methyleneblue molecules seem to decompose causing the decomposition of the eosin molecules in the photopolymer film.

Unfortunately the photosensitive system eosin/methyleneblue/Darocur 1173/styrene is thermally unstable. From *Figure 2* the thermal decomposition of the photosensitive dyes can be seen. The absorption spectra plotted in *Figure 2* indicate the simultaneous decay of the

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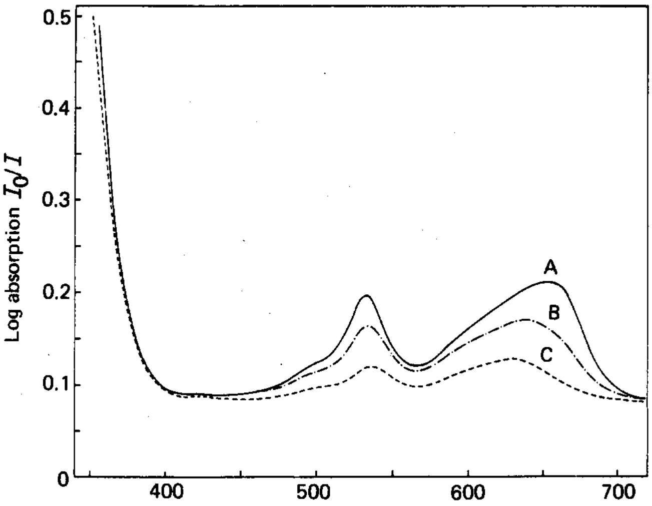

Figure 1 Absorption spectra of a 10 μm thick polymeric film on a u.v. glass substrate. The composition was: 30% PMMA/69.75% Darocur 1173/0.25% eosin–methyleneblue and residual solvent (chlorobenzene + styrene 80/20) in the 'as dried' state. A, film 'as dried'; B, after 15 min exposure; C, after 45 min exposure

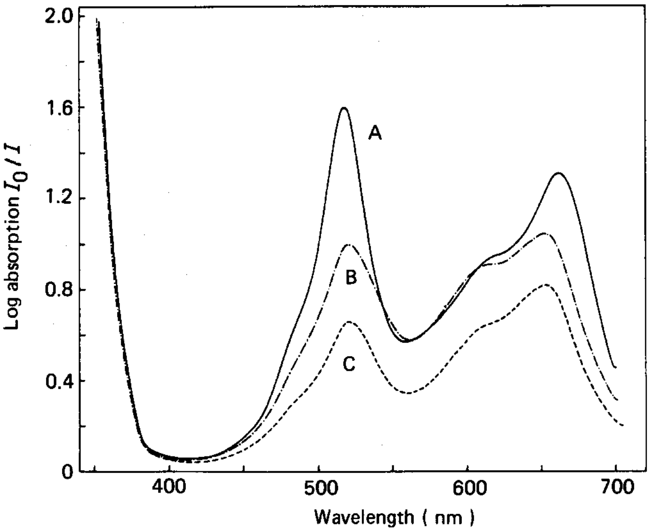

Figure 2 Absorption spectra of a solution of 0.004% (eosin–methyleneblue) + 1.6% Darocur 1173 in styrene measured in a 1 cm long optical u.v. glass cell. A, without annealing; B, after 1.5 h at 60°C without additional gas flow; C, after 1.5 h at 60°C with bubbling Ar gas through the cell

absorption peaks upon heat treatment. Curve B (no additional gas flow) and curve C (Ar) have been measured for the same annealing treatment. Clearly the thermal decomposition rate is lower in the presence of residual oxygen in the liquid.

Refractive index profiles

Polymer films coating u.v. glass substrates may be considered as planar optical waveguides and films coating Flint glass prisms with a refractive index $n_p > n_f$ may be treated as leaky waveguides[6]. The mode spectrum of these leaky waveguides can be measured for $n_p > N_0, N_1 \ldots$ with the effective mode indices N_m, by measuring the coupling angles θ_m. The TE modes are governed by the wave equation for the E_y component[7]:

$$d^2E_y/dx^2 = (N^2k^2 - n^2(x)k^2)E_y \qquad (1)$$

with x perpendicular to the film plane, k = wavevector of the incident light in a vacuum, $n(x)$ = refractive index perpendicular to the film plane, E_y = electric field component in the y direction (*Figure 3*).

Qualitative approach. The wave equation (1) has the same form as the time-independent one-dimensional Schroedinger equation with N^2 essentially corresponding to eigenvalue energy levels and $n^2(x)$ to the potential energy well, $V(x)$ (see ref. 8 for example).

For a constant, infinite $V(x)$ (square well potential) the eigenvalues levels are proportional to m^2, with $m = 1, 2, \ldots$ Comparison with the wave equation (1) leads to $n^2(x)$ = constant with $(N^2–C)$ proportional to m^2, i.e. for a constant refractive index of the film, the plot of the square mode indices N_m^2 *versus* m^2 should fit a straight line. The analogy to the infinite square well potential as a limiting case holds for thick polymer films and for the index steps at the film boundaries being large.

A second limiting case for a profile may be discussed by comparing the harmonic oscillator problem of quantum mechanics[8] with the corresponding parabolic refractive index profile of the polymer waveguide[7].

$$n(x)^2 = n_f^2(1 - x^2/2x_0^2) \qquad (2)$$

Again the analogy is good for small values of x, where the parabolic profile is not distorted by the film boundaries. The solutions to the wave equation (1) with the parabolic profile equation (2) are given by[7]:

$$N_m^2 = n_f^2 - (m + 1/2)(2n_f/kx_0) \qquad (3)$$

In *Figure 4* the measured mode spectra are plotted for the exposed (1e) and unexposed (1u) planar polymer waveguide after illumination and after subsequent annealing treatments. During the annealing procedure the residual solvent, the styrene monomer and the intermediate solvent Darocur penetrate the film surface and evaporate. Thus the film refractive index decreases overall. In the unexposed area the thermal decomposition of the photoinitiator leads to a radical polymerization of the residual monomer. The resulting refractive index change is not constant in the perpendicular direction x because the photoinitiator is dissolved in Darocur, which is moving towards the surface. From curves 1u, 2u and 3u in *Figure 4a* it can be seen that the mode indices N_m^2

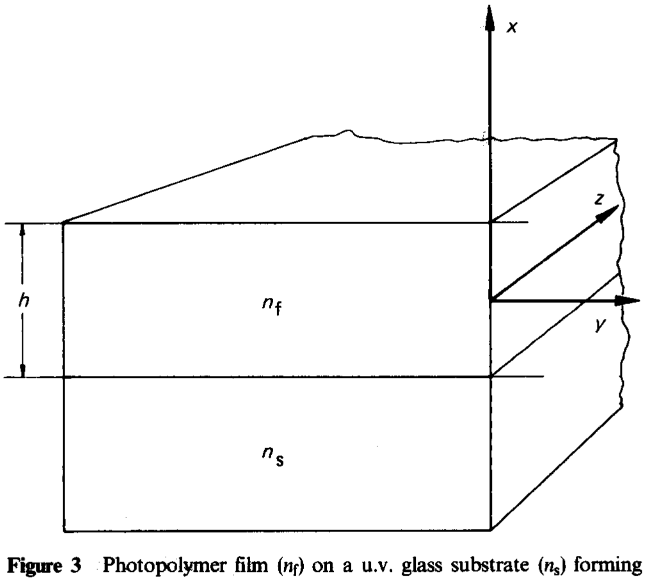

Figure 3 Photopolymer film (n_f) on a u.v. glass substrate (n_s) forming a planar optical waveguide

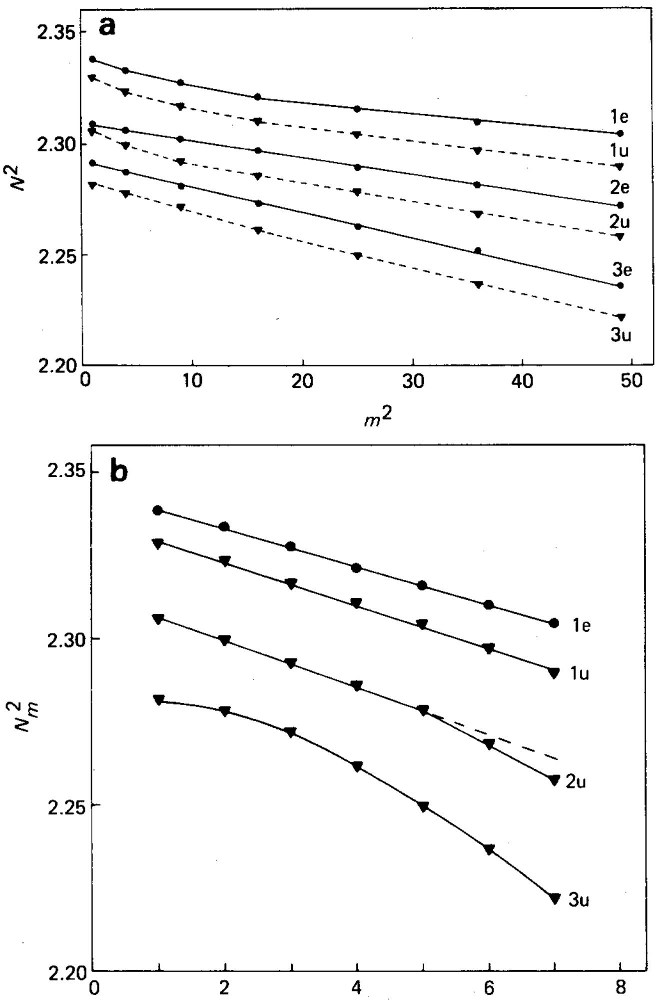

Figure 4 Measured mode spectra (a, N_m^2 *versus* m^2; b, N_m^2 *versus* m) for a *ca.* 20 μm thick photopolymer film of the same composition as described in the experimental section. Curve 1u: unexposed; curve 1e: exposed for 100 min with 0.8 mW/cm^2; curves 2: after annealing for 2 h at 60°C; curves 3: after additional 16 h at 60°C and 3.5 h at 80°C. The indices 'e' and 'u' indicate the exposed and unexposed film areas, respectively. Experimental error bars are of the order of the plotted dot sizes ($N^2 = \pm 0.001$)

deviate from a straight line, indicating a profile for $n^2(x)$. This profile 'moves' deeper into the mode spectrum during the thermal treatment. The products of the thermally indiced styrene polymerization diffuse into the film causing the $n^2(x)$ profile to broaden. On curve 2u, (*Figure 4a*) only N_1^2 and N_2^2 deviate from the straight line ($n^2(x)$ = constant), while in curve 3u the first four squared mode indices N_m^2 show smaller deviations.

In *Figure 4b* the square values of the measured mode indices N_m^2 are plotted as a function of the mode order m. For curves 1e and 1u a straight line is a good fit for the N_m^2 values, indicating that the mode spectra for the exposed and for the unexposed film may be fitted by equation (3).

Quantitative description. The plots in *Figure 4* and the discussion in the previous section lead to the result that refractive index profiles are present and that they change during the annealing procedure. To get a quantitative picture of the actual refractive index pattern we applied the inverse WKB (Wentzel–Kramers–Brillouin) method. This method allows calculation of $n(x)$ from the measured mode spectrum[9]. The WKB approximation may be used by assuming the index profile either to decrease monotonically from the surface or to be symmetrical in the case of a buried guide. We calculated $n(x)$ for both cases. Assuming a buried $n(x)$ profile we obtained the parabolic profiles with the maximum value in the middle of the film.

In *Figure 5* the results for $n(x)$ were obtained assuming a monotonically decreasing index from the surface. The surface index, which has to be estimated applying the inverse WKB method, was determined from the corresponding plots in *Figure 4*. The $n(x)$ curves may be described by a Fermi type function. This type of profile is already present in the unexposed film (▲). The profile is almost unchanged by exposure (●), except for the fact that the film in the unexposed area obviously shrinks during exposure. The mode spectra were both measured after the illumination. A further shrinkage of the film by the annealing procedure can be seen from the lower curve (○) in *Figure 5*. The Fermi function also becomes steeper, approaching a step index profile (see also *Figure 4a*). The explanation for the formation of the Fermi type refractive index profile may be given by the out-diffusion of the high index Darocur 1173. The profile already exists in the unexposed film and is not introduced by any exposure and it disappears with the complete out-diffusion of the Darocur upon annealing[5].

Light-induced refractive index changes

The exposure time was chosen to be high in order to reach saturation of the photochemical reaction (*Figure 1*). The mode spectra N_m^2 *versus* m^2 and N_m^2 *versus* m for the exposed and unexposed film are almost parallel (curves 1e and 1u). Also the actual refractive index profiles calculated from the mode spectra indicate the same Fermi type profile. Thus it can be deduced that the actual distribution of photoinitiator and monomer was 'photolocked'[10] by exposure to HeNe laser light.

In the exposed area the index profile can be changed into a step index profile, while the Fermi type profile in the unexposed area also becomes steeper. In this area the process is more complicated because, in addition to the diffusion of the reaction products (short chain styrene oligomers), there is the thermal decomposition of photoinitiator producing some additional radicals.

The refractive index changes achieved by HeNe laser exposure are exemplified in *Figures 4* and *5* with $\Delta n = 2 \times 10^{-3}$ after exposure and $\Delta n = 4 \times 10^{-3}$ after annealing. The Δn values obtained depend on the amount

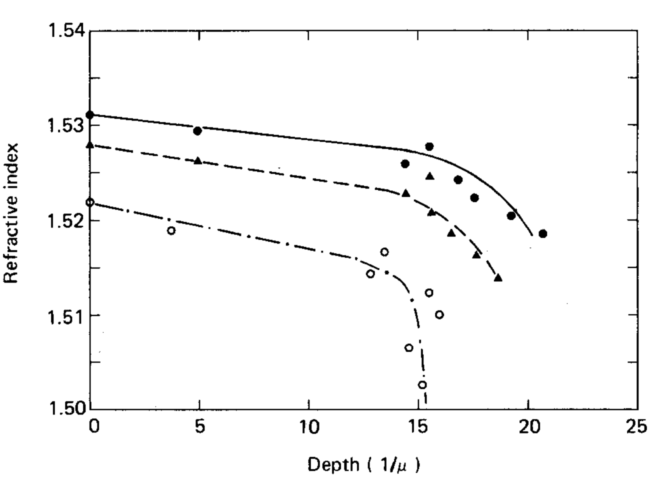

Figure 5 Calculated refractive index profiles: (▲), unexposed (see curve 1u in *Figure 4*): (●), exposed for 100 min with 0.8 m W/cm^2 (curve 1e in *Figure 4*): (○), after additional annealing for 2 h at 60°C (see curve 2u in *Figure 4*)

of residual monomer present in the polymer film at the time of exposure. The best values achieved for this system were $\Delta n = 6 \times 10^{-3}$.

From the level of index change it can be concluded that there is no significant influence of the intermediate solvent Darocur 1173 on the mechanism of refractive index change. The order of magnitude of Δn is comparable with the values obtained for simple styrene-doped PMMA films exposed to u.v. light[4].

Using methyleneblue alone, without eosin as a photoinitiator gives similar results. The photoinitiator can be decomposed by HeNe radiation and can also be decomposed thermally. However, the Δn values achieved by exposure to red light were lower as compared with the methyleneblue/eosin system as shown in *Figure 6*. After exposure there was no detectable difference between the exposed and unexposed areas. The subsequent annealing procedure leads to a small Δn value, which was mainly governed by the difference in the $n(x)$ profiles (curves 2u, 2e in *Figure 6*).

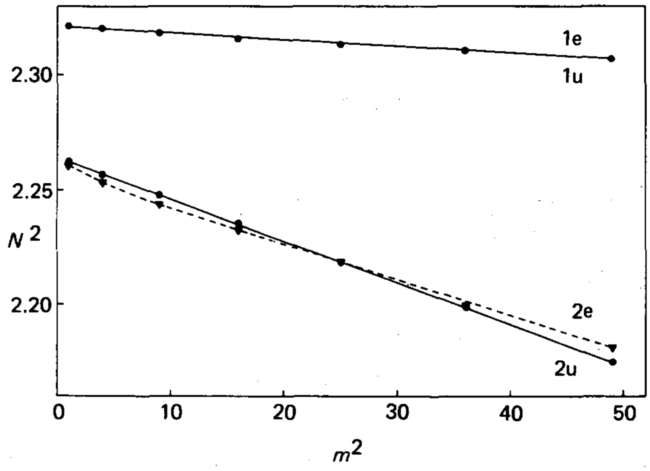

Figure 6 Measured mode spectra (N_m^2 *versus* m^2) for a photopolymer film (20 μm thick) of composition as described in *Figure 1* except for the photoinitiator consisting of methyleneblue only, without eosin. Experimental error bars are of the order of the plotted dot sizes ($N^2 = \pm 0.001$)

CONCLUSIONS

The use of methyleneblue/eosin as a photoinitiator system in the intermediate solvent Darocur 1173 leads to obtainable refractive index patterns in PMMMA-based polymer films, recorded with red light. After exposure the resulting $n(x)$ profile may be described by a Fermi type profile. Annealing treatment leads to a thermally fixed refractive index pattern and the profiles are changed towards step index profiles. Any remaining absorption losses in the red due to residual photoinitiator may be important for any potential uses that these patterns may have for integrated optics. Additional u.v. exposure of the patterns leads to complete decomposition of residual dyes.

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