Organic Materials for Real-Time Holographic Recording

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Photoactive organic layers, such as photochromic polymers and photopolymers, are investigated for real-time and in-situ holographic recording. The results with photochromic polymers containing spiropyran and spirooxazine dyes revealed that variations in the UV beam excitation and visible recording beam procedures significantly changed the exposure sensitivity and diffraction efficiency. These effects were exploited for all-optical modulation of the holographic gratings and explained by the photochemical and thermal transformations between photochromic stereoisomers. Copolymers of the photochromic spiropyrans were investigated for optical recording with infrared laser radiation at 10.5 and 10.6 μm. Although the recording primarily occurs by thermal bleaching, some nonthermal IR processes are also involved. Holographic recording in photopolymer layers, based on acrylamide monomers dissolved in polyvinylalcohol, is influenced by chemical additives. Specifically, a superadditive sensitization effect of diphenyl iodonium chloride together with triethanolamine significantly increased the exposure sensitivities at 514 nm, by a factor of more than 3 (to about 15 mJ/cm^2). Several formulations produce large enough refractive index modulations so that very high diffraction efficiencies (DE > 90%) are obtained. For certain conditions, under highly asymmetric recording angles, the diffraction efficiency is significantly reduced, and was found to originate from fringe bending due to nonlinear shrinkage. The introduction of crosslinking and gelling agents stabilize the formed grating structures against dimensional distortions.

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Introduction

Materials that can be exploited for in-situ and real-time optical holographic recording have been investigated for many years.[1–5] These include photorefractive materials,[6] photothermoplastics, photochromics, and photopolymers,[7] all of which have some advantages, but also some limitations.[8] For example, photorefractive crystals are erasable and have unique nonlinear optical properties, but have only moderate diffraction efficiency (DE) and show destructive readout; photothermoplastics have relatively high exposure sensitivities and are erasable, but have only moderate DE and high scattering noise; photochromics have high resolution and are erasable, but have relatively low exposure sensitivities and DE; finally, photopolymers have excellent DE and noise properties, but are not erasable and have moderate exposure sensitivities.

In this article, we consider two classes of organic photoactive polymer materials for real-time and in-situ holographic recording, with emphasis on the investigations conducted at the Weizmann Institute of Science.[9–17] The first class includes erasable organic spirocompound dyes that because of their photochromic nature can be colored with UV radiation, then bleached by visible light or by heat. The second class involves self-developing photopolymers that are based on acrylamide monomers dissolved together with xanthine dyes in polyvinylalcohol.

The investigations on the photochromic polymers were conducted to determine what factors influence exposure sensitivities. Holographic recording in the visible revealed that variations in the excitation and recording procedures significantly affect the exposure sensitivities.[9] Photokinetic modeling indicates that this effect originates from optical addressing of different photochromic stereoisomers.[10,11] The relatively fast photochromic transformations

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enables all-optical modulation of the holographic gratings by UV beam modulation.[9] In addition, the photochromic materials are considered with respect to optical recording with infrared laser radiation. This is of particular interest, because few real-time materials are available that possess suitable resolution capabilities in the IR. Our investigations consider both the contributions of thermal bleaching and nonthermal processes at 10.5 and 10.6 μm.[12,13]

The investigations on the photopolymeric recording system emphasize the influences of chemical additives on the holographic recording process. These include superadditive sensitization by triethanolamine (TEA) and diphenyliodonium chloride (DPI-Cl),[15,16] binder and other matrix effects on refractive index modulation and exposure sensitivity,[15,16] and matrix crosslinking on shrinkage, which in turn affects the diffraction efficiency (DE) and angular bandwidth of the holographic gratings.[17] With such photopolymers it is possible to obtain very high DE of more than 90%.

Photochromic Polymers

Basic Characteristics. Photochromics are chemical compounds that undergo reversible photochemical transformations.[18,19] The potential of photochromics for optical memory applications have already been investigated in the early 1950s.[20,21] These early investigations triggered worldwide research and development to exploit photochromic materials in a wide range of applications.[18,19,22] A very important advantage of photochromic materials is that they need no chemical or physical development so they can be exploited for in-situ optical recording. Moreover, the recorded information can either be permanently stored or erased for repeated recordings. When used for optical recording, two characteristics of photochromics are important. One is its thermal (dark storage) stability and the other its exposure sensitivity.

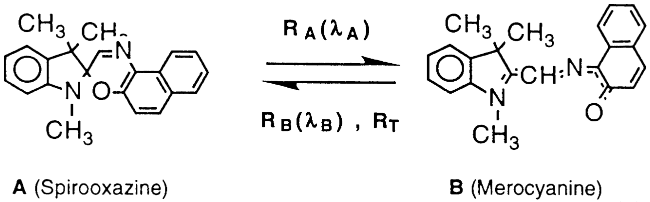
The thermal stability depends both on the compound itself and very critically on the environment.[23] In photochromic dye-polymer blends, the stability is mainly determined by the free volume distribution of the polymer matrix, which in turn is influenced by its rigidity. A good indicator for predicting the matrix rigidity, and thereby the thermal photochromic stability, is the glass transition temperature T_g of the polymer. A good correlation has been found[23] between the decoloration rate at a given temperature and the difference in temperature from T_g. Typically, in photochromics of simple dye-polymer blends, the thermal stability is often not high enough for optical storage. Fortunately, when the dye is incorporated as a copolymer and the dye concentration is increased, a much higher stability can be achieved. For example, the thermal stability of the colored merocyanine form of spiropyran copolymers increased, probably due to merocyanine dye aggregation.[23] Dye aggregation was indicated by shifts in the spectral absorption bands and by inhomogeneous thermal decoloration.

The exposure sensitivity of photochromic systems depends on the photochemical and thermal reaction kinetics, which in turn depend on spectral absorption cross section, quantum yield, wavelength of excitation, temperature, concentration, and solvent of the photochromic compound.[18,19,22] Although extensive investigations were conducted on the photochromic transformations in spirocompounds, many of the mechanistic aspects are still not completely understood. Specifically, data on the quantum yields of the photochemical transformations from the colored merocyanine to the colorless spirocompounds are relatively limited.[18,19,22] This stems from the complex nature of photochemical transformations. On one hand, these include several excited transitions that may differ significantly for different compounds. On the other hand, these photochemical tranformations are in competition with thermal transformations. Therefore, the pure photochemical parameters are very difficult to determine.

Several organic and inorganic photochromic media were investigated in the past as recording materials for holography.[24–28] Unfortunately, their exposure sensitivities were very low, typically more than 1 J/cm^2, so they are not practical for real-time applications. our recent investigations on real-time holographic recording in photochromic spirooxazine and spiropyran doped polymer thin films revealed that the exposure sensitivity could be significantly increased by chosing the proper optical recording procedure.[9,14] In this article, we show how the temporal holographic response and exposure sensitivity of such photochromic doped polymers are influenced by these procedures. We also show how in such a procedure it is possible, by modulating an external UV excitation beam, to correspondingly modulate holographically recorded gratings.[9]

At wavelengths longer than about 1 μm, the exposure sensitivity of conventional materials usually drops very rapidly, because, the absorption of radiation does not cause a change in the electronic levels, which could, in turn, induce primary photochemical reactions. Therefore, suitable materials that can record at long wavelengths in the IR, are very scarce. An alternative approach for recording in the IR uses thermally activated reactions. Chemical bond dissociation or association are thermally activated through vibrational excitation. For example, the conversion of spiropyran to merocyanine (coloring) is known to be thermochromic and the back conversion (bleaching) of merocyanine to spiropyran is thermally activated.[18,19] Therefore, the absorption of thermal radiation should, in principle, leave a permanent optical record in such systems. In this article, we consider the spiropyran bond for that purpose; specifically, recording of IR irradiation in colored spiropyrans is investigated.[12,13]

The Recording Mechanism. The photochemical and thermal conversion of photochromic dyes, such as spirooxazine and spiropyran derivatives, may be represented by the following simplified chemical equation, as



A (Spirooxazine) **B** (Merocyanine) (1)

where A and B are the colorless and colored stable forms, R_A and R_B are their photochemical rate constants, λ_A and λ_B are their excitation wavelengths, and R_T is the thermal rate constant of B to A. In solid polymers, the thermal conversion from A to B may be neglected.[18–22] In Eq. 1, B may be a mixture of several stereoisomers[18–22,29–32] of the merocyanine (MC) form and their aggregates.[23,33]

To explain the temporal holographic recording in our photochromic materials, we used[19] a semiempirical approach describing a closed system of one independent rate equation with the overall rate constants indicated in Eq. 1. We also assumed that a pseudo-first-order process with linear intensity dependence adequately describes the present photochromic system.[19] These are reasonable assumptions, because, first, relatively low optical densities are involved ($OD < 1$), and, second, low-light powers are applied, so that nonlinear effects from multiphoton absorption can be neglected.[10,11] The overall change in concentration of B with time, can then simply be given by the following rate equation

$$-dB/dt = R_B B - R_A A + R_T B = R_B B - R_A A_0 + R_A B + R_T B, \quad (2)$$

where A_0 is the total concentration of all the dye species, satisfying $A_0 = A(t) + B(t)$.

Integration of Eq. 2 with respect to B and t, yields a general solution given by[10,11]

$$B(t) = {C_1}\!/\!{C_2}\left\{1 - \exp(-C_2 t)\left[1 - {C_2}\!/\!{C_1}\, B(0)\right]\right\}, \quad (3)$$

where $C_1 = R_A A_0$, $C_2 = R_A + R_B + R_T$, and $B(0)$ *is* the concentration of B at $t = 0$. Equation 3 represents the time dependency of B, exposed simultaneously to all photochemical and thermal processes, as indicated in Eqs. 1 and 2. The photochemical processes are characterized by their respective rate constants, which for species i, is given by

$$R_i = I_i F_i \varepsilon_i \phi_i (\lambda_i / Nhc), \quad (4)$$

where

I_i = the light intensity (in joules $\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$) at wavelength λ_i
F_i = a photokinetic factor that corrects for absorption
ε_i = the decadic molar absorption coefficient [or cross section in cm^2/ mol]
ϕ_i = the quantum yield
N = Avogadro's number
h = Planck's constant
c = the speed of light.

For some exposure configurations, not all the processes will be active (I_i, $F_i = 0$), and Eq. 3 can be simplified. The photokinetic factor in Eq. 4 is usually not a constant, because the absorbance is time dependent. However, here the time dependency of absorbance can either be neglected or corrected for by normalization.[10,11]

When B is exposed to an interference pattern between two plane waves at λ_B, a cosinusoidal spatial modulation of concentration in the x direction $B(x)$ will be formed and thereby recorded as the holographic grating. Temporal holographic recording will therefore consist of a time-dependent spatial modulation $B(x,t)$, because

$$B(x,t) = B_0(t) + B_1(t)\cos(2\pi x/d), \quad (5)$$

where $B_0(t)$ and $B_1(t)$ are the average and the peak of the (time-dependent) spatial modulation in concentration [in $\mathrm{mol/cm}^3$], respectively, and d is the grating period. The gratings are recorded in the photochromic materials as a spatial modulation in absorbance. The time-dependent modulation is thus

$$a(x,t) = 2.303\varepsilon_B B(x,t), \quad (6)$$

where ε_B is the absorption coefficient at the readout wavelength. The readout radiation can in principle also lead to photochemical interactions. Therefore, to minimize destructive readout, the readout powers have to be significantly lower than those of the recording beams. The temporal diffraction efficiency DE(t) for our photochromic materials, i.e., for thick amplitude gratings,[34] is

$$\mathrm{DE}(t) = \exp(-2a_0(t)L/\cos\theta)\ \sinh^2(a_1(t)L/2\cos\theta), \quad (7)$$

where $a_0(t)$ is the (time-dependent) average absorbance, $a_1(t)$ is the amplitude of the absorbance modulation, L is the grating thickness, and θ is the readout angle.

Experimental Procedures. We investigated two photochromic polymer material systems.[14] The first involved simple spiropyran- or spirooxazine–polymer blends. These were prepared as follows: commercial poly (methylmethacrylate) (PMMA) was purified by recrystallization from tetrahydrofuran solutions. We used either a synthetized spiropyran dye[35] of 1-(β–hydroxyethyl)-3,3-dimethyl-6'-nitrospiro[indoline-2,2'-[2H–1]benzopyran] (dye Ia) dissolved in PMMA-toluene solutions at 10 wt% per PMMA or a spirooxazine dye, commercially available (from Aldrich), of 1,3,3-trimethyl-spiro[indoline-2, 3'-naphtoxazine] (compound A in Eq. 1).

The second involved photochromic copolymers. These were prepared as follows: a spiropyran monomer of 1-(β-methacryloxyethyl)-3,3-dimethyl-6'-nitrospiro[indoline-2,2'-[2H-1]benzopyran] (dye Ib) was synthesized as described elsewhere.[35] Then, free radical copolymerizations of the spiropyran monomers with methylmethacrylate (MMA), at given spiropyran concentrations, were performed.[36] The purified photochromic polymers were then dissolved in tetrahydrofuran and coated on glass slides or KBr spectroscopic windows to yield thin film layers of 6 to 9 μm.

The optics setup for recording and readout of simple holographic gratings is schematically shown in Fig. 1. Three separate and independent light sources were used. The first provided an incoherent excitation beam at λ_A = 364 nm from a UV lamp. The second provided two coherent plane waves for recording at λ_B = 514 nm from an argon ion laser. The third provided a readout beam at 633 nm from a He-Ne laser. The recording beams were incident at angles of ±30° with respect to the normal of the recording plane, so the spatial frequency was about 2000 lines/mm. The He-Ne beam was incident at the Bragg angle of 37°, and its power was kept sufficiently low (0.5 mW/cm^2) to minimize destructive readout. The readout beam was modulated by a mechanical chopper, referenced into a lock-in ampliflier (LIA), and the diffracted He-Ne beam was detected by a Si photodetector connected to the input of the LIA. The output from the LIA was connected to a digital storage oscilloscope and a computer for monitoring and data collection of the diffracted beam power. The excitation and recording exposure times were electronically controlled by mechanical shutters.

Three different recording procedures were used. In procedure (a), the photochromic layers were initially exposed to a homogeneous and incoherent excitation beam at λ_A = 364 nm, until maximal coloring occured. The initial exposure was then being followed by a simultaneous exposure to the two coherent recording beams at λ_B = 514 nm and to the UV excitation beam. At this stage of the exposure, the holographic interference pattern, created by the two coherent beams, is recorded by bleaching of the colored MC molecules, while, at the same time, new MCs are being formed by the homogeneous UV beam. In procedure (b), the photochromic layers were again initially exposed to the homogeneous and incoherent excitation beam at λ_A = 364 nm, until maximal coloring occured. The initial exposure was then followed by a separate exposure to the two

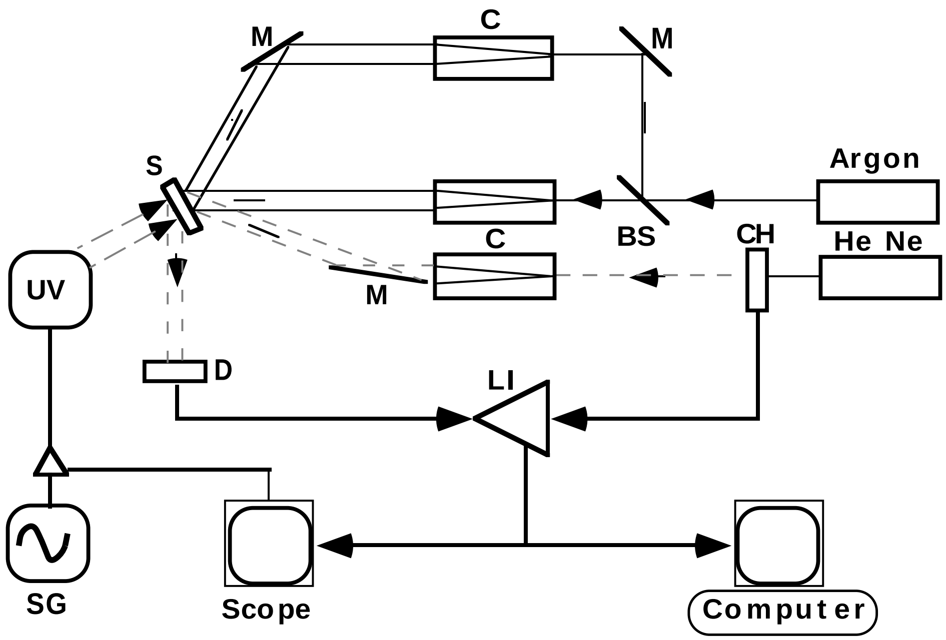


Figure 1. Schematic of the optics setup for holographic recording and readout: SG—signal generator, UV—mercury lamp, D—Si photodetector, S—sample, M—mirror, C—collimators and spatial light filters, BS—beamsplitter, CH—chopper.

coherent recording beams at λ_B = 514 nm (from an argon ion laser). At this stage of the exposure, the holographic interference pattern, created by the two coherent beams, is recorded by bleaching of the colored MCs only. Finally, in procedure (c), the photochromic layer was first simultaneously exposed to the homogeneous UV excitation beam and to the two coherent recording beams. This was immediately followed by an additional exposure to the two recording beams only. At this stage of the exposure, the initially recorded holographic grating is enhanced by a further bleaching of the colored MCs.

Results and Discussion. Holographic gratings were recorded using the three procedures in the different photochromic materials, and the diffraction efficiency (DE) versus exposure time (holographic growth) was measured in real time at 633 nm. The results with the spirooxazine containing samples are presented in Fig. 2. As shown, significantly different holographic growth rates are obtained for the three recording procedures. With the most sensitive procedure (c), the exposure sensitivity, i.e., the exposure needed for maximum DE, was found to be 350 mJ/cm^2 for the spirooxazine doped layers. With the spiropyran doped layers the corresponding exposure sensitivity was 750 mJ/cm^2. The maximum achievable DE was higher with the spiropyran (–0.85%) than that obtained with the spirooxazine (~0.48%).[9,14]

The experimental results of Fig. 2 can be explained by using Eqs. 3, 4, 6, and 7, and the proper boundary conditions for each of the recording procedures.[10,11] For example, the calculated results indicate that the thermal and photochemical decoloration (bleaching) rate constants should be significantly higher for procedure (c) than for the other two procedures. Specifically, the photokinetic rate constants R_B increased from about 0.06 s^{-1} in procedures (a) and (b), to about 0.10 s^{-1} in procedure (c). The corresponding quantum yields ϕ_B, which were calculated according to Eq. 4, increased from about 0.09 to 0.16 Einstein/mol. The existence of two thermal and photochemical decoloration rate constants indicates that the simplified reaction scheme in Eq. 1 is not sufficient to explain the observed photochromic responses for all exposure configurations. A more suitable reaction scheme to explain the results of Fig. 2 may be given by

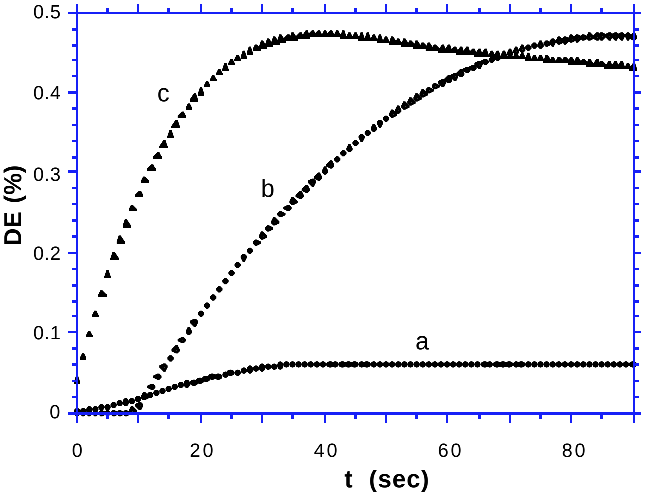


Figure 2. Real-time diffraction efficiency (DE) versus exposure time (t) of holographic gratings recroded at 514 nm in spirooxazine/PMMA films for three recording procedures (a), (b), and (c). Readout was at 633 nm. (a) initial exposure to the UV (364 nm) excitation beam of 5 mW/cm^2 and then simulatneous exposure to the UV beam and to the two recording beams of 9 mW/cm^2, (b) initial exposure to the UV beam and then separately to the two recording beams, (c) initial simultaneous exposure to all the beams followed by exposure to the two recording beams only.

$$A \underset{R_{B1}(\lambda_B),R_{T1}}{\overset{R_A(\lambda_A)}{\rightleftarrows}} B_1 \underset{R_{B2}(\lambda_B),R_{T2}}{\overset{k_{T1}}{\rightleftarrows}} B_2, \qquad (8)$$

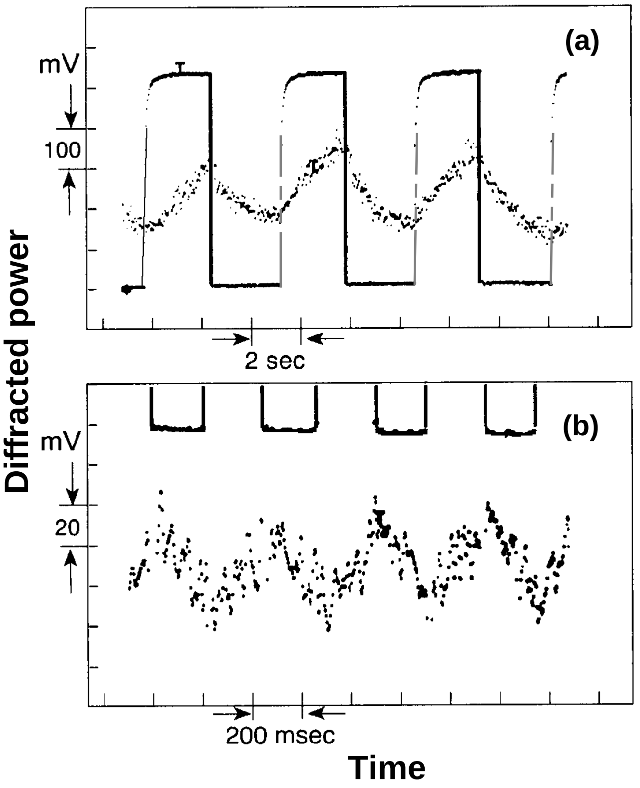


Figure 3. Modulation of holographic gratings (dotted traces) as a result of square wave modulation of UV beam (line traces). The modulated gratings were continuously exposed to the recording beams, each of 20 mW/cm^2, (a) with modulation frequency of 0.2 Hz, (b) with 2.5 Hz.

where B_1 and B_2 are now two different forms of the colored MC molecules, satisfying the relation $B = B_1 + B_2$; R_{B1} and R_{B2} or R_{T1} and R_{T2} are the respective photochemical or thermal rate constants for the transformations from B_1 to A and from B_2 to B_1, and kT_1 is the thermal rate constant for the transformation from B_1 to B_2. The reaction scheme in Eq. 8 suggests a consecutive conversion between A, B_1, and B_2. However, a parallel conversion between A and the two MC forms may also be considered. The exact identity of the two MC forms B_1 and B_2 cannot be derived from our investigations, but are most probably MC stereoisomers of different thermal and photochemical stability.[19,22,32]

The experimental results of Fig. 2 can now be interpreted in terms of the relative populations of the two MC isomers B_1 and B_2. With recording procedures (a) and (b), the photochromic film is initially exposed to the UV excitation beam alone so that at steady state, the more stable colored isomers B_2 will be dominantly populated. A subsequent exposure to the visible recording beams causes decoloration to A, with the rate-determining step being the transformation from B_2 to B_1 (and/or B_2 to A in a parallel scheme). With recording procedure (c), however, the initial exposure to all beams yields a mixture of all the species associated with the scheme of Eq. 8, with a significant population of B_1. Therefore, a subsequent exposure to the recording beams causes decoloration at a significantly increased rate, which is mainly determined by the transformation from B_1 to A.

Our results indicate that it should be possible to reversibly control the population of the photochromic isomers by optical addressing using the different recording procedures. Specifically, we found that the DE of holographic gratings recorded in the photochromic layers exhibit a significant increase when the UV excitation beam is shut off during the simultaneous exposure to the UV and recording laser beams. Yet when the layers are again simultaneously exposed to the UV and the recording beams, the DE is significantly reduced; in essence, the UV beam partially erases the gratings. Therefore, by modulating the UV excitation beam, it was possible to correspondingly modulate the holographically recorded gratings.[9,14] Figure 3 shows the results when the gratings were continuously exposed to the recording beams, each of 20 mW/cm^2, while the UV excitation beam was modulated. The modulated UV excitation square waves are also shown; their frequency was 0.2 Hz in Fig. 3(a) and 2.5 Hz in Fig. 3(b). The modulation amplitude M decreases with modulation frequency with M being given by $M = (I_{\max} - I_{\min}) / (I_{\max} + I_{\min})$. The photochromic layers doped with spirooxazine could be modulated at higher frequencies than the layers with spiropyran, as expected from their holographic exposure sensitivities.

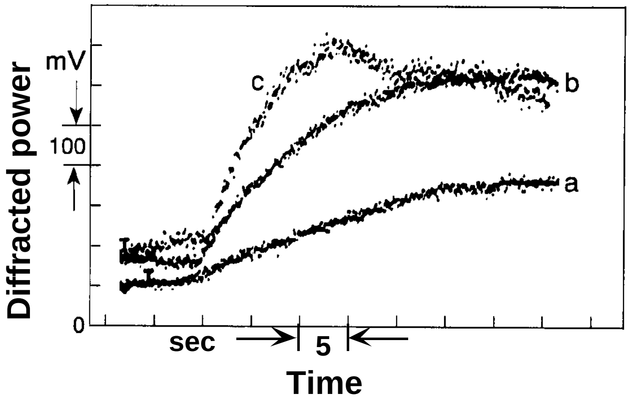
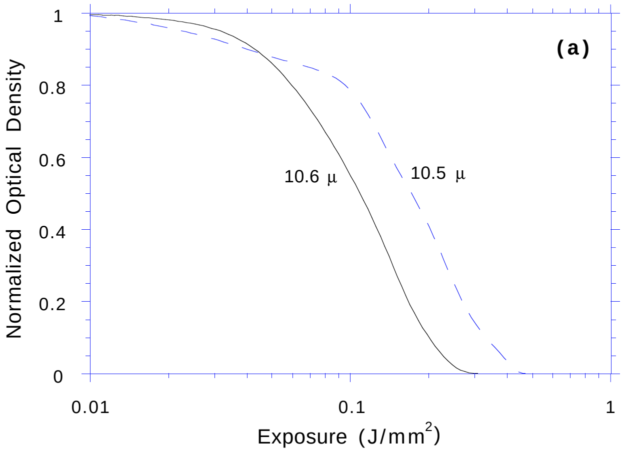


Figure 4. Temporal holographic growth in spirooxazine/PMMA for different recording beam intensities: (a) 10 mWcm^2, (b) 20 mW/cm^2, (c) 40 mW/cm^2. The UV excitation beam intensity was 10 mW/cm^2.

Figure 4 shows the dependence of the temporal holographic growth on the recording intensities. For these, we used the recording procedure of first simultaneously exposing the photochromic layers to both the excitation and recording beams and then separately to the recording beams. The results in Fig. 4 were obtained by maintaining the excitation beam at 10 mW/cm^2 and increasing each of the recording beams from 5 to 20 mW/cm^2. The temporal holographic growth increased when the recording beam intensities were increased, in accordance with our model predictions.[10,11] Similar increases in the temporal holographic growth were obtained by increasing the excitation beam intensity. In our experiments, the excitation and recording beam intensities were limited to 10 and 20 mW/cm^2, respectively, so that the holographic growth rates and the modulation frequencies were limited to about 0.5 sec^{-1} and about 5 Hz, respectively. These can be significantly improved by further increasing the excitation and recording beam intensities.

In related experiments, we investigated the feasibility of exploiting the spiropyran-PMMA copolymer films for recording at infrared wavelengths. Specifically, the photochromic polymer layers were first colored by irradiation from a UV lamp at 364 nm and exposure energy of 1 J/cm^2. The colored photochromic samples were then incorporated into



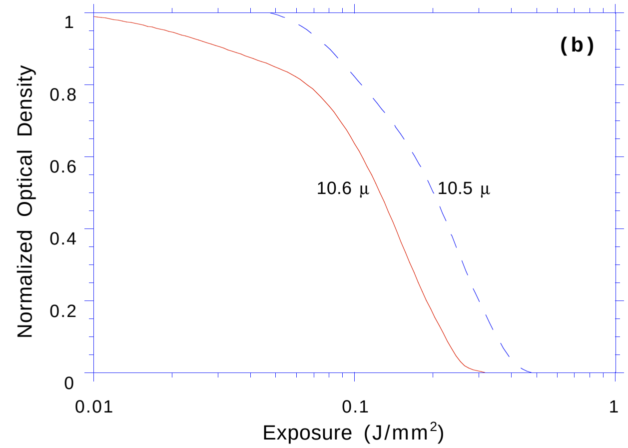


Figure 5. Normalized optical density as a function of absorbed IR exposure energy of spiropyran-MMA copolymer layers. The irradiation wavelengths were 10.6 and 10.5 μm from a CO_2 laser. (a) the spiropyran concentration is 6 mol %. (b) The spiropyran concentration is 25 mol %.

an optical setup very similar to that depicted in Fig. 1. However, in these experiments, a CO_2 laser rather than an Ar laser was used. The samples were simultaneously illuminated with one or two recording beams at 10.6 or 10.5 μm from the CO_2 laser and with a readout beam at 633 nm from a He-Ne laser.

The change in optical density as a function of absorbed exposure to the 10.6 and 10.5 μm lines of a CO_2 laser are shown in Fig. 5. The IR response is of the positive type, i.e., the optical density (OD) measured at 633 nm decreases as a function of the IR exposure. In other words, the laser radiation bleached the precolored merocyanine, thereby converting it back to spiropyran. A significant reduction in exposure sensitivity occurs for the samples exposed at 10.5 μm when compared to those exposed at 10.6 μm. Specifically, at 50% of the initial optical density, the exposure sensitivity was about 0.1 J/mm^2 at 10.6 μm wavelength and about 0.2 J/mm^2 at 10.5 μm. Note that the irradiations at 10.6 and 10.5 μm are absorbed in these spiropyran-containing layers to different degrees as indicated by IR spectroscopic data.[12,13] Specifically, a strong band at ~959 cm^{-1} (= 10.43 μm) was assigned to the nitrogen-spirocarbonoxygen (N–C-O) stretch vibration.[37] Therefore, the 10.6 μm (~941 cm^{-1}) laser line falls just outside that spiroband, whereas the 10.5 μm (~954 cm^{-1}) laser line falls well within that band.

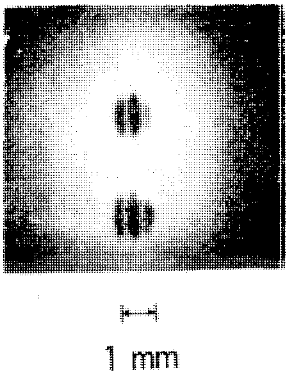


Figure 6. Interference patterns of two beams from a CO_2 laser recorded in a photochromic polymer film.

The results of Fig. 5 indicate that the absorbed IR energy is dissipated by a different mechanism at each of these two wavelengths. When thin organic layers are on top of a thick glass substrate, which represents a very efficient heat sink, small differences in thermal dissipation processes within the thin layers can be neglected. Therefore, the results in Fig. 5 in conjunction with the spectroscopic data[12,13,37] suggest that because the 10.5-μm radiation is essentially absorbed by the spiropyran molecules (because the –N-C-O– group does not exist in merocyanine), the thermal bleaching is retarded at 10.5 μm because of partial spiropyran to merocyanine reconversion (coloration). Such reconversion may be neglected at 10.6 μm, where the IR absorbance of the -N-C-O- group is much weaker. In other words, hot spiropyran molecules formed on absorption of 10.5-μm radiation are reconverted to merocyanine before the absorbed energy is dissipated into heat. Note that with organic solids, it is extremely difficult to measure differences in vibrational excitation and relaxation processes, because the intermolecular energy dissipation is normally dominant. Nevertheless, such wavelength-selective IR-laser-induced chemical reactions were observed in the gas phase.[38] Finally, the results of Fig. 5 also reveal that the exposure sensitivities are essentially independent of spiropyran concentrations; this indicates that the intermolecular merocyanine interactions and/or the degree of aggregate formation do not play a significant role within the concentration range we considered.

In other related experiments, we recorded in the photochromic polymers, the interference patterns of two planar beams derived from a CO_2 laser. A photograph of a representative recorded interference pattern is shown in Fig. 6. The distance between adjacent fringes was about 500 μm. We have also recorded focused CO_2 laser spots of about 25 μm diam, indicating that the resolution capability of our photochromic materials is equal or better than 40 lines/mm. This resolution is similar to that reported with chemically developed silver halide materials used for recording 10.6-μm radiation.[39]

Photopolymers

Basic Mechanisms of Recording. Photopolymers that undergo monomer polymerization when exposed to light are advantageous for optical holographic recording for several reasons. First, they are self-developing so the recording and readout can be done in situ and virtually real-time. Second, they store the recorded interference pattern as changes of the refractive index to obtain high diffraction efficiencies.[2,7,40,41] Third, they record on molecular level to obtain very high resolving power and low scattering noise. Yet the photopolymer materials have a number of drawbacks. These may include relatively poor exposure sensitivities (typically 1 to 3 orders of magnitude lower than silver halide emulsions), layer shrinkage as a result of exposure, and poor stabilites both before as well as after recording. Here we consider photopolymer formulations that can alleviate some of these disadvantages.

Three stages are involved during holographic recording in photopolymers. In the first stage, the incident light is absorbed by the photoinitiators (or photocatalysts—usually a photosensitizing dye and a charge transfer agent) to produce free radicals[42–44] that form monomer radicals.[42] In the second stage, monomer depletion in the exposed regions causes a concentration gradient that then induces monomer diffusion from the unexposed to the exposed regions.[43,45,46] In the third stage, termination occurs by radical recombination.

The exposure sensitivity is primarily determined during the first recording stage. In radical polymerization, charge transfer from the sensitizing dye to the monomer determines the rate (sensitivity) during initiation.[47] In hydrophilic acrylamide photopolymer systems with sensitizing dyes such as xanthines (e.g., eosin) and thiazines (e.g., methylene blue), toluenesulfinic acid,[42] amines, or acetyl acetone have been used as the charge transfer agents.[47] In hydrophobic polymer systems, iodonium salt derivatives have been studied as charge enhancing and transfer species.[48–50] The iodonium salts were initially found to induce cationic polymerization,[48] and later also to enhance radical polymerization.[49,50] The second and third recording stages also have some influence on the exposure sensitivity through the propagation and termination kinetics of polymerization, which may be diffusion controlled.[43,45,46] Diffusion of the monomer species are primarily influenced by the matrix parameters of the binder and plasticizers.

The diffraction efficiency (DE) is primarily determined during the second and third recording stages. Both surface relief modulation and/or volume refractive index modulation influence[42] the DE. These modulations are influenced by the compositions of monomers, binders, and other matrix additives. It has been found[50–52] that by controlling the refractive index of each component of a multicomponent polymer system, it is possible either to enhance or reduce the DE. For example, cross-linking agents influence the density of the matrix and thereby the refractive index.

In general, photopolymers include an acrylic-type monomer, differing mainly by the specific monomer species and by the binder and sensitizer compositions.[2,7] The early photopolymer recording systems for holographic recording as proposed in the late 1960s and early 1970s, were based on acrylamide solutions contained in recording cells.[42,47,53,54] Unfortunately, these systems had only moderate diffraction efficiencies, and poor preexposure, as well as postexposure stabilities. Some improvements were obtained by the addition of a binder, such as polyvinylalcohol (PVA), so the solutions could be cast and dried onto glass substrates.[55] Dried photopolymers had also been formulated for hydrophobic systems using cellulosic binders.[43,45]

Here, we consider acrylamide-PVA photopolymer formulations with additives that influence the exposure sensitivities, DE, and both temporal and dimensional stabilities. Specifically, we introduce iodonium salt sensitization into hydrophilic systems using diphenyliodonium chloride (DPI-Cl) in conjunction with eosin Y and TEA to significantly increase the exposure sensitivities.[15] We also consider the influence of the PVA binder parameters on the exposure sensitivity during real-time holographic recording.[16] Then, the influence of glutaraldehyde (GA) on the refractive index modulation and thereby on the DE are described.[16] Finally, to reduce layer shrinkage,[17] we add GA or $CuCl_2$, which are known to be efficient thermal crosslinking agents in hydrophilic polymers.[56]

TABLE I. Composition of Photopolymer Coating Solutions—For Detailed Description of Components See Text

Component	Mechanism	Concentration (M)
PVA	binder	1.136
DMSO	plasticizer	0.205
Acrylamide	monomer	0.446
BAA	crosslinking	0.026
Glutaraldehyde	crosslinking	2.5×10^{-3}
TEA	charge transfer	0.027
Eosin Y	photosensitizer	3×10^{-5}
DPI-Cl	charge transfer	13×10^{-5}

Experimental Procedures and Results. The chemicals used for the preparation of the photopolymer coating solutions were either hydrolyzed PVA from Aldrich (degree of hydrolization > 99%) of number averaged molecular weight $M_n \approx 89{,}000$, or PVA from Fluka of $M_n \approx 22{,}000$ (degree of hydrolization > 97%) or $M_n \approx 15{,}000$ (degree of hydrolization > 86%), and acrylamide (AA) from BDH (99.9%), N,N'-methylenediacrylamide (BAA) from Merck (99.5%), dimethylsulfoxide (DMSO) from Fluka (99.5%), triethanolamine (TEA) from BDH (99%), glutaraldehyde (GA) from Merck (25%, f.s.), eosin Y (2',4',5',7'-tetrabromofluorescein disodium salt) from Aldrich (94%) and diphenyliodonium chloride (DPI-Cl) from Fluka (99%). The composition of a typical coating solution is given in Table I. In some of the experiments, the concentrations of TEA and DMSO were varied simultaneously to keep the total plasticizer concentration at 2% by weight.

The photopolymers were coated by casting the solutions on leveled glass substrates and dried at controlled temperature and humidity for at least 48 h. The layer thickness was controlled by the concentration and/or the quantity of the coating solutions. The optics setup for evaluating the photoactive polymer layers was very similar to that shown in Fig. 1. In one set of experiments, the interference fringes were perpendicular to the recording layer, i.e., unslanted. In another set, the fringes were slanted, to evaluate the dimensional changes of the polymer gratings; here, the recording beams were incident at 0° and 60° with respect to the layer normal.

To study the influence of our charge transfer agents, photopolymer coatings containing either TEA, DPI-Cl, or both at a constant eosin Y level were prepared, and then exposed in the holographic setup. The results of the holographic response, i.e., DE versus exposure, are presented in Fig. 7. The simultaneous presence of both DPI-Cl and TEA significantly increases the exposure sensitivity compared to that of their individual responses. These experiments therefore clearly demonstrate the existence of a superadditive sensitization effect between the iodonium salt and triethanolamine in our hydrophilic photopolymer system; this finding is in agreement to a similar superadditive effect found in hydrophobic photopolymers.[49,50]

To elucidate the mechanism of the superadditive effect of our charge transfer agents, we seperately determined the influence of either the DPI-Cl or the TEA concentration; the results are presented in Figs. 8 and 9. Figure 8 shows the DE versus exposure response for

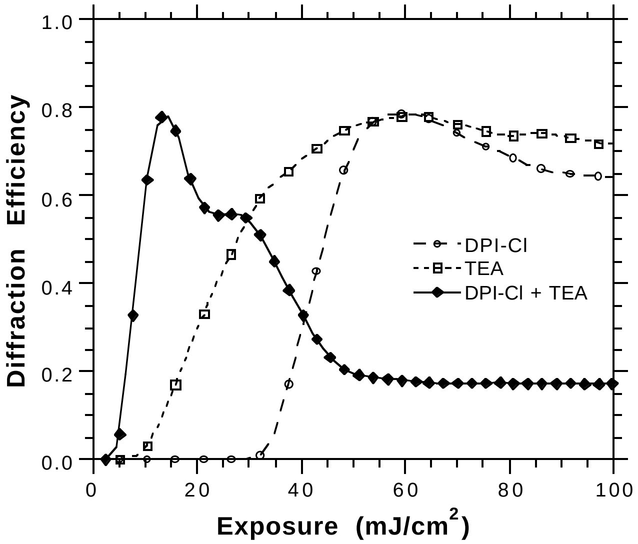


Figure 7. DE versus exposure of holographic gratings recorded at 514 nm in PVA-acrylamide photopolymers sensitized by eosin Y and different charge transfer agents: squares—TEA alone, circles—DPI-Cl alone; diamonds—TEA and DPI-Cl. Formulations are according to Table I.

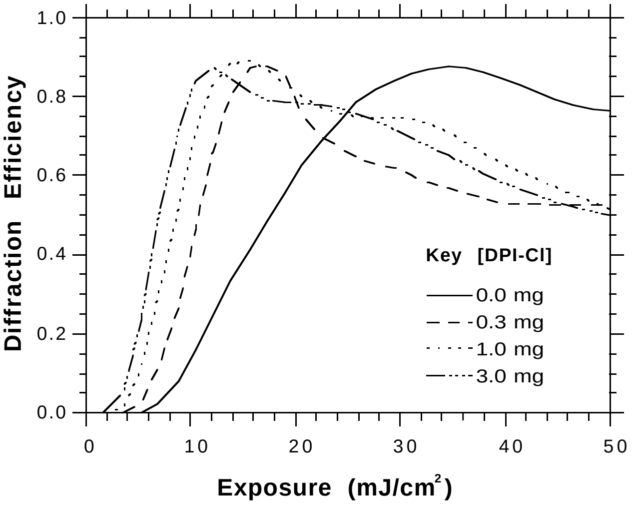


Figure 8. Diffraction efficiency versus exposure for different DPI-Cl concentrations and constant TEA concentration. Other parametes as for holographic grating of Fig. 7.

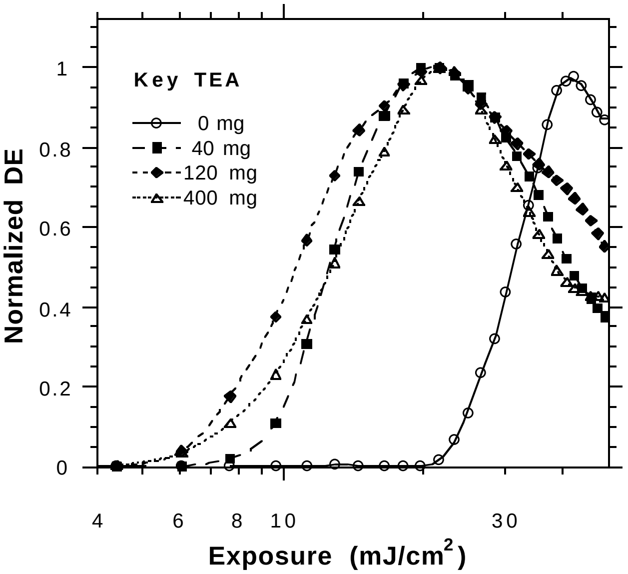


Figure 9. Normalized diffraction efficiency versus exposure for different TEA concentrations and constant DPI-Cl concentration. Other parameters are the same as for holographic gratings of Fig. 7.

different DPI-concentrations with the TEA and eosin Y concentrations kept constant. The addition of DPI-Cl significantly increases the exposure sensitivity; this increase continues with increasing DPI-Cl concentration to about 12 mg/100 cc of coating solution. Noteworthy is that sensitivity increases occur at all levels of DE, but are greater at larger DE levels. This indicates that DPI-Cl has a stronger effect during the propagation stage of polymerization than during the photoinitiation stage. The fact that the most effective concentration range of DPI-Cl is of the same order of magnitude as the photosensitizing dye eosin Y indicates that DPI-Cl is in some way interacting with the dye photoproduct.

Figure 9 shows the DE versus exposure response for different TEA concentrations with the DPI-Cl and eosin Y concentrations kept constant. The addition of TEA, in particular up to 120 mg/100 cc of coating solution, significantly increases the exposure sensitivity. Let us again consider the dependence of sensitivity on concentration at various DE levels. For concentrations of about 40 mg, the sensitivity increase is independent of the DE level. However, for concentrations higher than 120 mg, the sensitivity increase diminishes at large DE levels. This indicates that TEA has a stronger effect during the photoinitiation stage than the propagation stage of polymerization.

The results of Figs. 7 through 9 suggest that the superadditive effect between TEA and DPI-Cl is due to their complementary contributions during the photoinitiation stage and the propagation stage of polymerization. Specifically, TEA enhances the exposure response during photoinitiation, suggesting that TEA is more efficient in transferring the photoproduct of the dye to the monomers than is DPI-Cl. But DPI-Cl enhances the propagation stage indicating that the monomer/oligomer radicals are more stable against mutual recombination, thereby preventing termination at lower molecular weights. A higher degree of polymerization for each photon absorbed (increased quantum yield) leads to increased Δn for a given exposure, which in turn increases the holographic exposure sensitivity. Also interesting to note is that either DPI-Cl, TEA, or both together enhance the exposure sensitivity without affecting the maximal DE within experimental error.

Because we lacked complete data on transient and ground state photoproducts in our hydrophilic system, the precise reaction pathway of our photopolymer system cannot be delineated. Nevertheless, in light of the above results and data from polar hydrophobic systems,[49,50] we propose a mechanism[15,16] explained by the reactions between eosin, DPI-Cl, and TEA during the various stages. In the first stage, the photon-induced transitions of eosin[44,49] (E) occur between its singlet ground state E^1, and its singlet and triplet excited states E^{1*} and E^{3*}. In polar solvents, the triplet has been found to break down into two radical dye ions, namely the radical anion $E^{-\bullet}$ and the radical cation $E^{+\bullet}$. The chemical reactions suggest three possible contributions of DPI-Cl to the superadditive photopolymer kinetics, which are related to its strong interaction with the radical dye

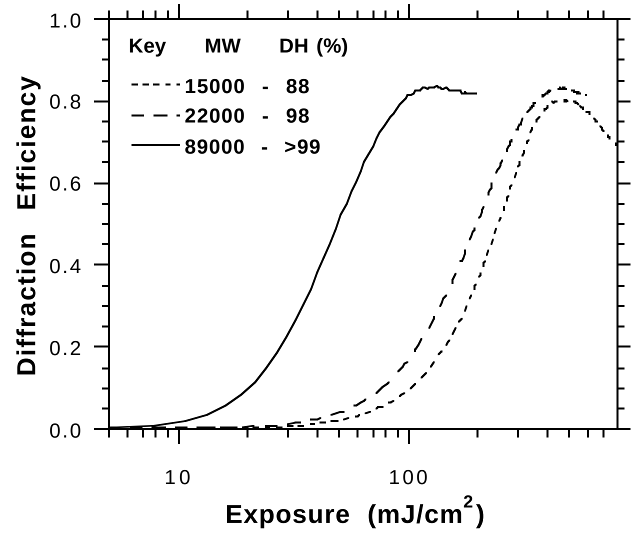


Figure 10. Diffraction efficiency versus exposure of holographic gratings recorded in photopolymer layers with PVA binders for different molecular weights (MW) and degrees of hydrolysis (DH).

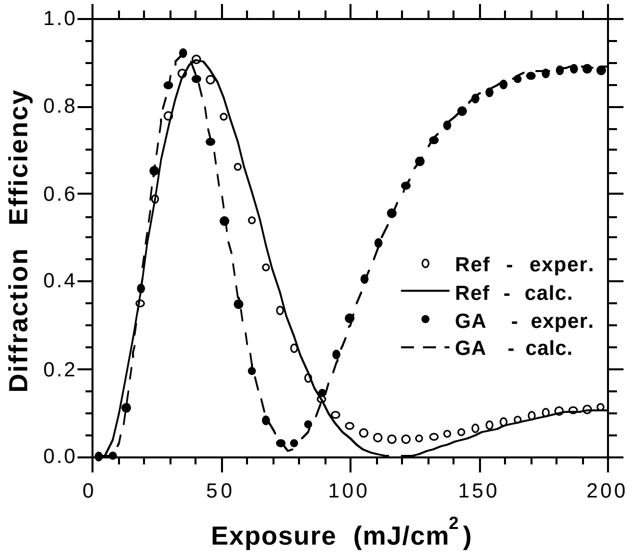


Figure 11. Exposure response of holographic gratings as in Fig. 9 as a function of PEA concentration at constant DPI-Cl concentration.

ions and TEA. First, the interactions between the excited triplet state of eosin and the iodonium species DPI-Cl initially result in excited diphenyl iodonium cation species, which further break down to a phenyl iodonium cation radical and a phenyl radical.[48,49] Consequently, the resultant radical species of DPI-Cl may interact with triethanolamine, leading to its radical species TEA$^\bullet$; therefore, additional *TEA*$^\bullet$ formation increases the quantum yield of polymerization initiation. The second contribution of DPI-Cl is to enhance the propagation kinetics by diminishing the radical dye ion concentration, which are known to cause termination in radical polymerization.[49] The third contribution of DPI-Cl is by an increased concentration of photoinduced radical and cationic species, which in turn leads to the increased initiation of radical[50] or cationic polymerization.[48] Cationic polymerization would also reduce termination and thereby increase the holographic exposure response, because of electrostatic repulsion between positively charged species.

To investigate the influence of the matrix binder parameters, we prepared coating solutions according to Table I, containing PVA of various molecular weights (MW) and degrees of hydrolysis (DH). Holographic gratings were recorded in the coated photopolymer layers and evaluated in real-time. The results of DE versus exposure are presented in Fig. 10. The holographic response is significantly influenced by a change in the PVA binder. Specifically, the exposure sensitivities were improved by a factor of about 4 to 5 by increasing the MW (and DH) from about 15,000 (88%) to about 89,000 (>99%). This indicates that the diffusion coefficients are lower in the low-MW (low-DH) PVA binders than in the high-MW (high-DH) binder. While we are not certain about the precise mechanism of this matrix binder influence, we speculate that by increasing the MW (DH), the conformation of the photopolymerized polyacrylamide is affected, eventually leading to polymer phase separation.

Another class of additives that influence the binder matrix are crosslinking agents. For example, the photocrosslinking agent bisacrylamide stabilized the stored refractive index modulation, probably by a matrix densification mechanism.[15] To further assess the influence of cross-linking bonds to the binder matrix, we chose glutaraldehyde (GA) as the additive.[56] For this purpose, photopolymer layers with and without GA were prepared. Holographic gratings were recorded in these layers and evaluated. The results of DE versus exposure are presented in Fig. 11. The addition of GA significantly influences the DE response indicating that the refractive index response was correspondingly affected.

To determine the change of the refractive index modulation (Δn) as a function of exposure in our photopolymer layers, we used the experimental results of Fig. 11, and the theoretical diffraction efficiency relation for thick and unslanted volume phase gratings,[34] of

$$\eta = \sin^2 \frac{\pi \Delta n T_e}{2\lambda \cos\theta}, \qquad (9)$$

where Δn is the peak-to-peak amplitude of the refractive index modulation in the cosinusoidal grating, T_e is the effective grating thickness in the recording layer, λ is the free-space wavelength, and θ the readout angle at Bragg conditions with respect to the normal of the recording layer. The resultant Δn versus exposure responses are shown in Fig. 12. As can bee seen, the addition of GA to our photopolymer coatings significantly increases the dynamic range of Δn; specifically, the maximal achievable Δn was increased from 0.014 to 0.018. This indicates that GA causes more crosslinking in the exposed areas than in the unexposed ones and suggests the presence of polyacrylamide cross-linking by glutaraldehyde, which is known to react well with polyamides.[56]

The angular response of holographic gratings, i.e., DE as a function of angular deviation from the Bragg angle recorded in our photoactive polymer layers is shown in Fig. 13. The results are for both unslanted and slanted fringe orientations. The gratings with unslanted fringe recording orientation exhibit very high DE at Bragg conditions and show the expected sinc function which is in agreement with theory.[15,34] However, the gratings with slanted fringe recording orientation exhibit a significantly different angular response. Specifically, it shows asymmetric behavior with an additional sidelobe appearing at high

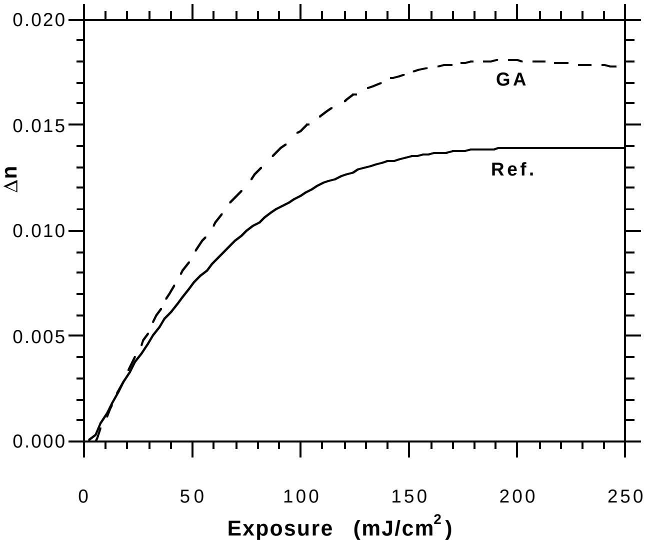


Figure 12. Calculated refractive index modulation as a function of exposure derived from data of Fig. 11 and using Eq. 9.

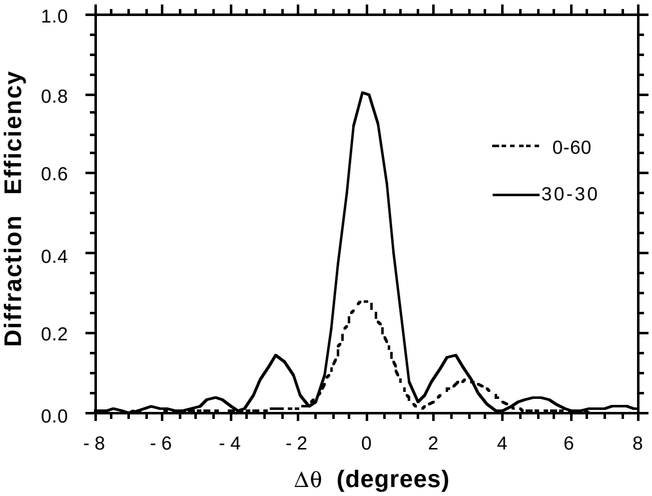


Figure 13. DE as a function of angular deviation from Bragg conditions of holographic gratings recorded in photoactive polymer layers with unslated (30-30) and slanted (0-60) fringe orientation.

angles. Also, the maximum DE at the Bragg angle is significantly reduced. This grating anomaly can best be explained by a nonlinear shrinkage mechanism that causes stress-induced fringe bending.[57] This is schematically illustrated in Fig. 14, where the straight fringes of the original layer thickness *D* bend to higher angles and shrink to reduced thickness *D*'. Such a model is consistent with both the observed lower DE as well as the asymmetric angular response.

To decrease shrinkage and the resultant grating anomalies in the photoactive layers, we investigated inorganic and organic cross-linking agents for increasing the tensile strength of the polymer matrices. The inorganic agent was cupric chloride ($CuCl_2$), which is a known gelation agent with PVA solutions,[56] and the organic agent was glutaraldehyde, which cross-links both through hydroxyl as well as through amide groups.[56] For this purpose, polymer coating solutions were prepared according to the composition in Table I with an additional 16 mg $CuCl_2$/100 ml or with an additional 400 mg glutaraldehyde/100 ml coating solution.

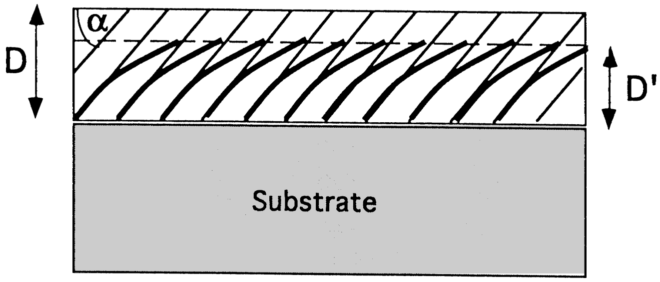


Figure 14. Schematic representation for the effect of nonlinear shrinkage in holographic gratings recorded in photoactive polymer layers.

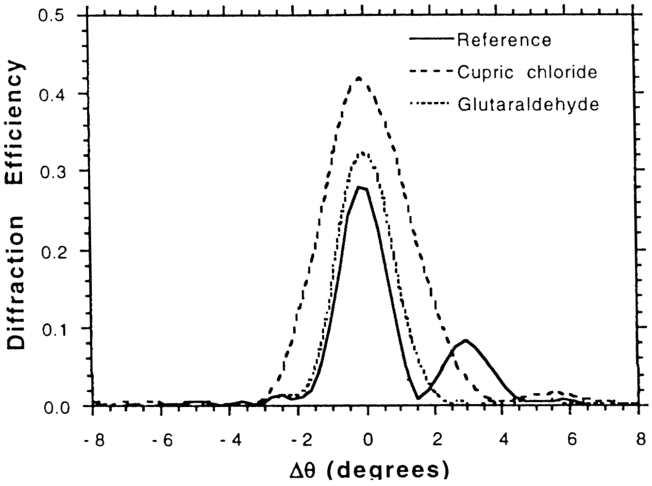


Figure 15. DE versus angular deviation from Bragg conditions for holographic gratings recorded with slanted fringe orientation in photoactive polymer layers with or without crosslinking agents.

We then recorded and evaluated holographic gratings in the resultant polymer layers. The results of the angular response for the slanted fringe geometry are shown in Fig. 15; also shown for reference are the results for layers with no cross-linking agents. The incorporation of cross-linking agents improved the angular response of slanted holographic gratings, but the improvement is not sufficient. So further investigations with new additives are needed.

Conclusions

We have shown that organic polymer layers doped with photochromic spirooxazine and spiropyran dyes can be exploited for in-situ and real-time holographic recording. Furthermore, we have shown that all-optical modulation of the holographically recorded gratings was achieved by modulating a UV excitation beam. We found that the temporal holographic growth is influenced by the specific UV excitation and visible recording beam procedures. Specifically, the exposure sensitivities and modulation frequencies strongly depend on the recording procedure and on both the excitation and recording beam intensities. In our experiments, the maximal excitation and recording beam intensities were limited so that the holographic growth rates and the modulation frequencies were limited to about 0.5 s^{-1} and about 5 Hz. However, these could be further improved by increasing the excitation and recording beam intensities. The holographic results can be explained with our model by thermal and photochemical transformations between colorless spirooxazine and at least two stereoisomeric forms of colored MC.

Precolored photochromic spiropyran copolymers were also exploited for optical recording in the infrared. We found that the recording is predominantly due to thermal bleaching. However, as revealed by changes in exposure sensitivity with a small change in the CO_2 laser wavelength (from 10.5 to 10.6 μm), some non-thermal IR processes can also contribute during the recording. In related experiments, the interference pattern and focused spots derived from a CO_2 laser were recorded; the resolution capabilities were found to be at least 40 lines/mm.

We showed that holographic recording at 514 nm in our photopolymer layers occurs in real-time and in-situ, meaning that they are self-developing. The hydrophilic photopolymer formulations are based on acrylamide monomers dissolved together with a sensitizing xanthine dye (eosin) and charge transfer agents in polyvinyl alcohol. Specifically, we added the charge transfer agent diphenyl iodonium (DPI) salt together with triethanolamine (TEA). The addition of DPI significantly increases the exposure sensitivities from about 35 to 12 mJ/cm^2, i.e., by a factor of about 3, without affecting the maximal obtainable diffraction efficiency (DE). The sensitivity increases are shown to originate from a superadditive effect between TEA and DPI. The mechanism of this superadditivity is explained by the reactions between the sensitizing dye and the charge transfer agents. These include charge transfer from the eosin dye triplet to DPI, thereby reducing termination of photopolymerization by dye radical ions. The iodonium reaction products are radicals that transfer their electronic charge to TEA; an increase in the free radical concentration of TEA increases the quantum yield of polymerization initiation.

The possible influences on the holographic storage mechanism by other additives to the photopolymer formulations such as cross-linking agents were also investigated. Our formulations basically produce large enough refractive index modulations so that very high diffraction efficiency (DE > 90%) can be obtained when the recording beam angles are symmetric. The addition of glutaraldehyde further increases the dynamic range of refractive index modulation from 0.014 to 0.018. In certain cases, DE significantly drops when recording angles are highly asymmetric. The origin of this effect is shown to stem from grating anomalies in that the slanted fringes bend due to nonlinear shrinkage effects during recording, as expressed by highly asymmetric angular DE responses. The present investigations show that the introduction of crosslinking and gelling agents stabilize the formed grating structures against dimensional distortions. Specifically, the introduction of cupric chloride or glutaraldehyde into our photoactive polymer layers had the effect of reducing the asymmetric angular DE response. Further investigations and a more precise analysis and control of this effect are still needed with respect to possible photonics applications such as holographic grating couplers.

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