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Optical Materials 27 (2005) 1567–1570
OPTICAL Materials
www.elsevier.com/locate/optmat

Real-time holographic gratings recorded by He–Ne laser in polymer films containing spirooxazine compounds pre-irradiated by UV light

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Received 28 June 2004; accepted 22 October 2004
Available online 15 December 2004

Abstract

Real-time holographic gratings were optically recorded with a pair of interferential He–Ne laser beams (632.8 nm) in poly(methylmethacrylate) (PMMA) film containing 6′-piperidino-1,3,3-trimethylspiro[indolino-2,3′-[3H]naphtha-[2,1-b][1,4]oxazine] (SO-1) pre-irradiated by ultraviolet light. The transformation from SO-1 to photomerocyanine (PMC) was studied in detail. PMC was observed in two forms. The holographic characteristics of the recorded gratings were dependent on the polarization direction of the recording beams. Reversible holograms were recorded in the medium by modulating UV light.

PACS: 42.70.L; 78.20.W
Keywords: Holographic recording; He–Ne laser; Spirooxazines; UV-light irradiation

1. Introduction

Spirooxazines (SOs) are a class of photochromic compounds closely related to spiropyrans (SPs). Among spiro-compound Os are of particular interest due to their fatigue resistance and photostabilitywhich provides the possibility of practical applications in lenses of variable optical density, displays, filters, and optical-storage devices [1–7]. Photochromism in SOs arises from carbon–oxygen (C_{spiro}–O) bond cleavage in the colorless spiro form upon UV-light excitation and subsequent isomerization to colored open forms, called photomerocyanines (PMCs). PMCs can revert to the spiro forms thermally or photochemically. Hence, it is possible to perform holographic recording with visible light for SOs pre-irradiated by UV light. Previously, most studies of optical information storage with SOs employed UV, Ar or CO_2 lasers as the writing beams. Optical storage can also be accomplished with the 632.8 nm line of a He–Ne laser for Methyl-Orange-doped polyvinyl alcohol films pre-irradiated by an Ar laser [8,9] and for push–pull azo dye accompanied by 532 nm irradiation [10]. However, little attention has been paid to optical storage with SO compounds using polarized red wavelength lasers (e.g. He–Ne), which is practical for real-time applications.

In this work, holographic gratings were recorded with 632.8 nm He–Ne laser light in poly(methyl methacrylate)

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0925-3467/$ - see front matter
doi:10.1016/j.optmat.2004.10.012

(PMMA) films containing 6′-piperidino-1,3,3-trimethylspiro[indolino-2,3′-[3H]naphtha-[2,1-b][1,4]oxazine] (SO-1). The transformation from SO-1 to PMC was studied in detail. A correspondingly modulated holographic grating was obtained by modulating the UV light.

2. Experimental

2.1. Materials and preparation

The chemical structures of 6′-piperidino-1,3,3-trimethylspiro[indolino-2,3′-[3H]naphtha-[2,1-b][1,4]oxazine] (SO-1) and the corresponding UV-induced photomerocyanine (PMC) are shown in Fig. 1. SO-1 was synthesized with microwave irradiation [11]. The structure of the compound was tested by FT-IR and ^{1}H NMR. From the FT-IR spectrum, a few bands can be identified: 2963 cm^{-1} (S=C–H), 1613 cm^{-1} (m, C=N), 1183 cm^{-1} (m, C–O–C). ^{1}H NMR measurements were also carried out using a Bruker DMX-400 instrument operating at 400 MHz. ^{1}H NMR spectrum also indicated (CD_3SOCD_3, δ, ppm): 1.35(6H, $2\times CH_3$), 1.84(6H, $3\times CH_2$), 2.75(3H, N–CH_3), 3.04(4H, $2\times$ N–CH_2), 8.5–8.7(10H, AR-H). Commercially available (PMMA) was used without further purification. Both SO-1 and PMMA were dissolved in $CHCl_3$ and then cast on a clean glass substrate. After the solvent evaporated slowly, the composite film was obtained and used for the measurement of the holographic recording. The pre-set dye concentration was 5.0 wt% and typical film thickness was 10 ± 1 μm measured with a Precision Ellipsometer.

2.2. UV–vis measurements

Fig. 2a and b illustrate the UV–Vis spectra of PMMA films containing SO-1 and PMC obtained with a Perkin-Elmer Lambda 900 spectrophotometer in the range of 190–3200 nm. The absorption bands at 365 nm correspond to π−π* electronic transition for both SO-1 and PMC, while the absorption near 633 nm corresponds to n–π* electronic transition and intermolecular charge-transfer of PMC [12].

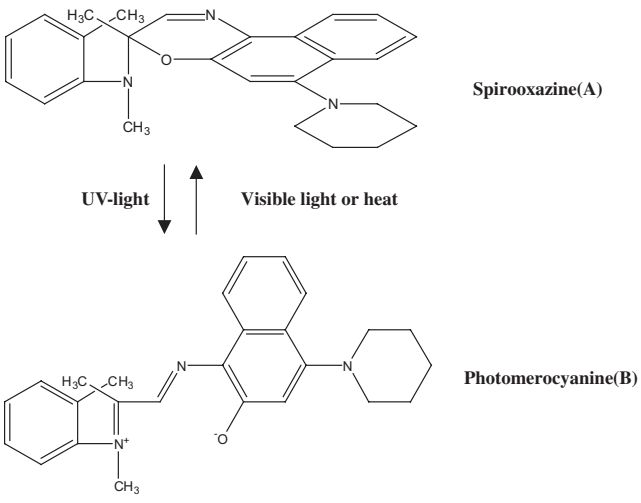


Fig. 1. Chemical structure of SO-1 and corresponding UV-induced PMC form.

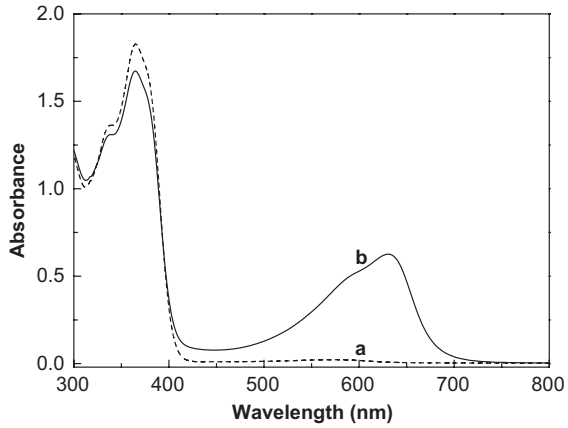


Fig. 2. (a) UV–Vis spectrum of PMMA film doped with 5 wt% SO-1; (b) the corresponding spectrum after UV-induced isomerization of SO-1 to PMC.

2.3. Optical setup

Holographic recording measurements were made possible by two interferential laser beams irradiating the sample, as shown in Fig. 3. The major elements of the experimental setup were a linearly polarized He–Ne laser (632.8 nm) which generated the writing and reading beams. A half-wave plate was used to rotate the polarization of the He–Ne beam. The diameter of the laser beams was ~0.3 cm, and the intersecting angle between the beams was ~10°. A mercury-arc lamp (125 mW) was used to irradiate the sample with homogenous, incoherent light at 365 nm. The diffractive signals were registered on a CCD camera interfaced with a computer.

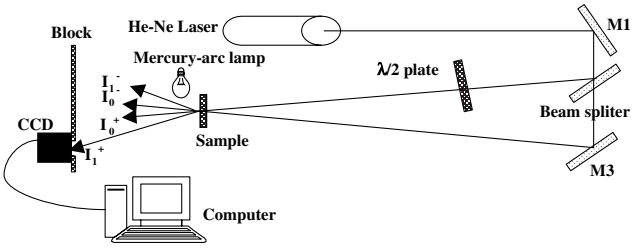


Fig. 3. Experimental configuration for the recording of holographic gratings by two He–Ne laser beams, where M denotes a mirror, P a polarizer, CCD a charge coupled device (sensitive region from 350 to 900 nm).

3. Results and discussion

Fig. 4 shows the first-order diffractive signal of the holographic gratings generated by two He–Ne laser beams with the same (s, s) polarization. The power density of each beam was 10/0.07 mW/cm^2. The experimental sequences are described as follows: first, the film was exposed to UV irradiation until maximal coloring was observed. Then, as illustrated in Fig. 4, with the UV source on, the two linearly polarized He–Ne beams irradiated the sample and the intensity of the measured diffractive signal showed a rapid increase to a maximal value in a few seconds and then decreased gradually to a fix value (marked as point A). When one He–Ne beam was switched off with the UV source on, the diffractive-signal intensity increased sharply again and decreased further approaching a constant value at point B.

Based on the experimental observations, the possible explanation may be suggested as in Scheme 1, where **A** is SO-1, $\mathbf{B_1}$ and $\mathbf{B_2}$ are two different forms of the colored PMC molecules [3,13,14], $R_{\mathbf{B1}}$ and $R_{\mathbf{B2}}$ or R_{T1} and R_{T2} are the respective photochemical or thermal rate constants for the transformations from $\mathbf{B_1}$ to **A** and from $\mathbf{B_2}$ to $\mathbf{B_1}$, and R_{T12} is the thermal rate constant for the transformation from $\mathbf{B_1}$ to $\mathbf{B_2}$. Prior to time zero shown in Fig. 4, the photochromic film was exposed only to UV light and the more stable colored isomers $\mathbf{B_2}$ were expected to be the dominant form. As the power density of He–Ne laser beams was much greater than that of the mercury-arc lamp (about 1 mW/cm^2), the observed peak maximum of the diffractive signal is attributed to the decoloration to **A** upon irradiation by the He–Ne beams. After approximately one minute, **A** was transformed to a mixture of all the species associated with the Scheme 1 with a significant population of $\mathbf{B_1}$ owing to the synthetical effect of He–Ne laser beams and UV light. The first equilibrium was reached at point A where only one He–Ne beam was switched off. Here, both the bright and dark regions of the interference fringe in the polymer film were exposed to one He–Ne laser beam and the UV light. $\mathbf{B_2}$ in the dark region was transformed to **A** immediately as the result of He–Ne irradiation, while the mixture of all the molecules in the bright region remained. Consequently, the second peak appeared. However, UV light drove the transformation of **A** to $\mathbf{B_2}$ until the second equilibrium is reached at point B, after approximately 1 min.

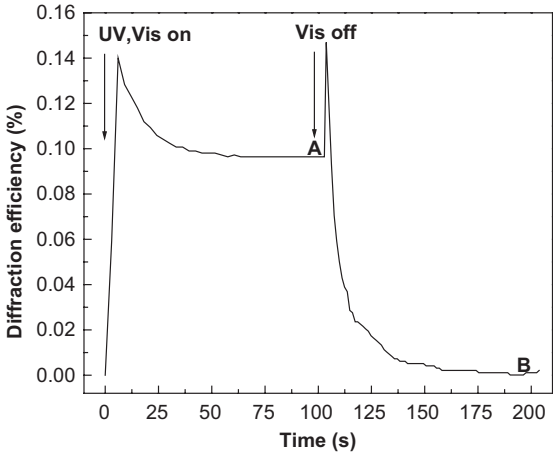
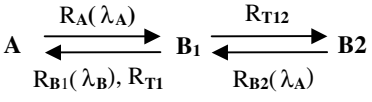


Fig. 4. The first-order diffractive signal of the holographic gratings pre-irradiated by UV-light versus time. "On" means UV-light or visible light (He–Ne laser beam) is turned on and "off" means UV-light is turned off.



Scheme 1.

Fig. 5 compares the first-order diffractive signals recorded by two He–Ne beams with and without UV irradiation in the same (s, s) polarization, and without UV irradiation in different (s, p) polarization (curve 1, 2 and 3, respectively). For curve 2 and 3, films were initially exposed to UV excitation until maximal coloring occurred, then subsequently exposed to the two recording beams (10 mW, respectively). Since PMC has a much larger polarity than SO-1 [15–17], the diffractive signal of s,p-gratings (curve 3) indicates reorientation of PMC molecules irradiated by a linearly polarized He–Ne beam. At the same time, the He–Ne laser induces transformation from PMC to SO-1, which causes the population of PMC molecules to decrease, which results in the weakest diffractive signal for s,p-gratings relative to that of s,s-gratings with or without UV irradiation. s,s-gratings are formed by both the isomerization from PMC to SO-1 and the orientation of PMC molecules [18]. With UV irradiation (curve 1), the diffractive signal

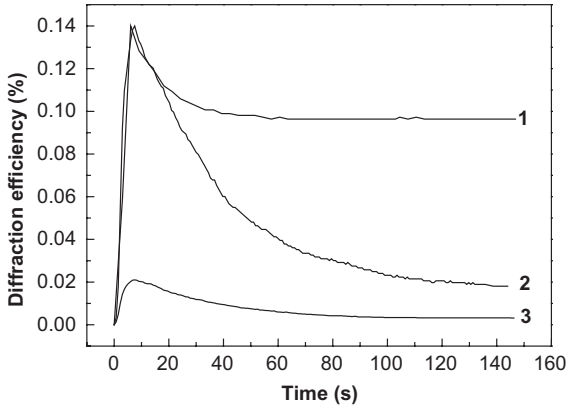


Fig. 5. The first-order diffractive signals of the holographic gratings recorded by two He–Ne beams versus time with and without UV irradiation in the same (s, s) polarization, and without UV irradiation in different (s, p) polarization (curves 1, 2 and 3, respectively).

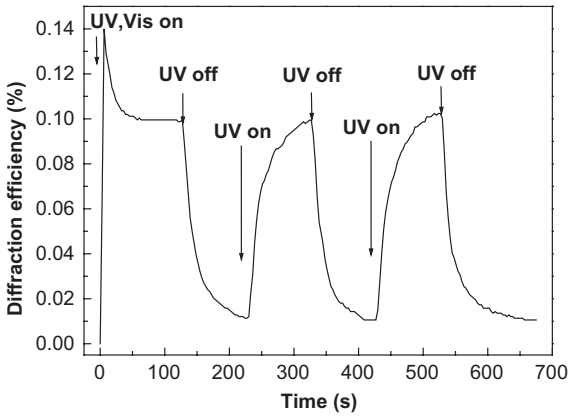


Fig. 6. Holographic gratings modulated by UV-light. "On" means UV-light or visible light (He–Ne laser beam) is turned on and "off" means UV-light is turned off.

at equilibrium states is caused by both the isomerization from $\mathbf{B_2}$ to $\mathbf{B_1}$ and the orientation of $\mathbf{B_1}$; without UV irradiation (curve 2),the diffractive signal at time ~150 s is mainly caused by the isomerization from $\mathbf{B_2}$ to **A**. So the diffraction efficiency of s,s-gratings without UV irradiation is lower than with UV irradiation.

With such a strong effect of UV light on the diffractive signals, it was possible to correspondingly modulate the holographic recording gratings by modulating the UV excitation. Fig. 6 shows the sample that was pre-irradiated by UV light until maximal coloring occurred. Then, as marked at time zero, with the UV source still on, the He–Ne laser beams were turned on. When the equilibrium value of the diffractive-signal intensity was reached, the UV light was turned off. All the molecules in the bright region were transformed to **A** as a result of He–Ne irradiation and also randomized thermally. Thus, the contribution of orientation gratings decreased and the diffractive-signal intensity decreased. When the UV light was turned on again, the diffractive-signal intensity increased to the prior equilibrium value. As shown in Fig. 6, this phenomenon can be repeated many times with little deterioration. Thus it has potential to be used for optical-switching.

4. Conclusion

Real-time holographic gratings of 6′-piperidino-1,3,3-trimethylspiro[indolino-2,3′-[3H]naphtha-[2,1-b][1,4] oxazine pre-irradiated by UV light were recorded by He–Ne laser of 632.8 nm. The holographic characteristics of the recorded gratings were related to the polarization direction. The holographic recording gratings were repeatably modulated by UV light through several cycles. The spirooxazine-doped polymer film allowed multiple uses without apparent fatigue.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (60176003), the Foundational Excellent Researcher to Go beyond Century of Ministry of Education of China, and Science Foundation for Young Teachers of Northeast Normal University.

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