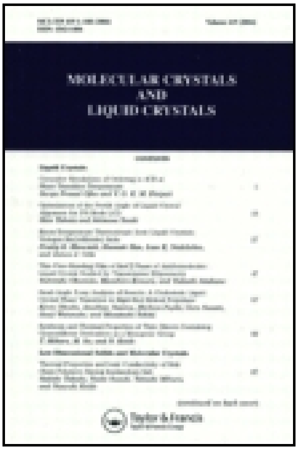


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Temporal Holographic Response in Photochromic Polymer Films

V. Weiss [a] , V. A. Krongauz [b] & A. A. Friesem [a]

[a] Electronics Department, The Weizmann Institute of Science, Rehovot, Israel, 76100

[b] Organic Chemistry Department, The Weizmann Institute of Science, Rehovot, Israel, 76100

Version of record first published: 24 Sep 2006.

To cite this article: V. Weiss , V. A. Krongauz & A. A. Friesem (1994): Temporal Holographic Response in Photochromic Polymer Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 367-370

To link to this article: http://dx.doi.org/10.1080/10587259408037845

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 367–370
Reprints available directly from the publisher

Printed in the United States of America

TEMPORAL HOLOGRAPHIC RESPONSE IN PHOTOCHROMIC POLYMER FILMS

V. WEISS*, V. A. KRONGAUZ** AND A. A. FRIESEM*
*Electronics Department and **Organic Chemistry Department
The Weizmann Institute of Science, Rehovot, Israel 76100

Abstract A photokinetic model for elucidating the holographic recording mechanism in photochromic polymers is presented. Holographic recording in the visible range by bleaching of precolored material is emphasized. The predictions for three different exposure configurations agree well with the experimental responses of holographic gratings recorded in spirooxazine containing polymer films. The holographic response changes significantly with variations in the exposure configurations, indicating that the thermal and photochemical transformations occur between colorless spirooxazine and two stereoisomeric forms of the colored dye.

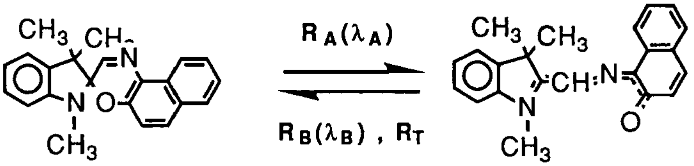
INTRODUCTION

Recent investigations on real-time holographic recording in photochromic spirooxazine and spiropyran doped polymer thin films revealed that the temporal holographic response critically depended on the optical recording configurations, and on the UV excitation and visible recording beam intensities[1].

In this paper, we present a photokinetic model for elucidating the holographic recording mechanism in photochromic polymers. The model predictions for three different recording configurations are compared to the experimental responses of holographic gratings recorded in spirooxazine containing polymer films. The experimental and calculated results are discussed in terms of the transformations between the colorless spiro-compound and its colored merocyanine (MC) dye.

PHOTOKINETIC MODEL

The photochemical and thermal conversion of photochromic dyes, such as spirooxazine and spiropyran derivatives, may be represented by the following simplified chemical equation[2,3], as



(1)

A (Spirooxazine) **B** (Merocyanine) 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[2,3]. B in Eq. (1) may be a mixture of several stereoisomers[2-6], of the merocyanine (MC) form and their aggregates[2,7].

The overall change in concentration of B with time, can simply be given by the following rate equation

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

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

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

where $C_1 = R_A A_0$, $C_2 = R_A + R_B + R_T$ and $B(0)$ is the concentration of B at $t = 0$.

When B is illuminated with an interference pattern at λ_B , a spatial modulation of concentration $B(x)$ will be formed and recorded as the holographic grating. We assume that our photochromic gratings consist essentially of a spatial modulation in absorbance, so that the time dependent modulation is $a(x,t) = 2.303\ \varepsilon_B\ B(x,t)$, where ε_B is the absorption coefficient at the readout wavelength. The time dependent modulation depth, which is twice the modulation amplitude, and similarly, the modulation average, are determined by

$$2B_1(t) = B(t)_{min} - B(t)_{max}; \quad 2B_0(t) = B(t)_{min} + B(t)_{max}, \qquad (4)$$

where $B(t)_{max}$ and $B(t)_{min}$ are the concentrations obtained in the regions of maximum and minimum intensity of the interference pattern.

The temporal diffraction efficiency of the thick amplitude gratings can now be given as

$$DE\ (t) = \exp\ (-2a_0(t)\ L\ /\ \cos\theta\ )\ \sinh^2(\ a_1(t)\ L\ /\ 2\cos\theta), \qquad (5)$$

where $a_0(t)$ and $a_1(t)$ are the (time dependent) average and amplitude of the absorbance modulation, respectively, L is the grating thickness and θ is the readout angle[8].

RESULTS AND DISCUSSION

In order to verify our proposed model, we performed holographic recording experiments with polymethylmethacrylate (PMMA) films containing 10 wt.% of compound A (see Eq. (1)). The details of film preparation and of the holographic set-up are described elsewhere[1]. The temporal DE (holographic growth) was measured in real-time at 633 nm by a He-Ne laser. Figures 1(a) - 1(c) show the normalized calculated and experimental DE response and the calculated color decay for the three exposure configurations (a), (b), and (c). In config. (a), the initial exposure to the UV (364 nm) excitation beam of 5 mW/cm^2 is followed by a simultaneous exposure to the UV beam and to the two recording beams each of 9 mW/cm^2; in config. (b), the initial exposure to the UV beam is followed by a separate exposure to the recording beams; in config. (c), an additional exposure to the recording beams only, immediately follows the simultaneous exposure to all the beams.

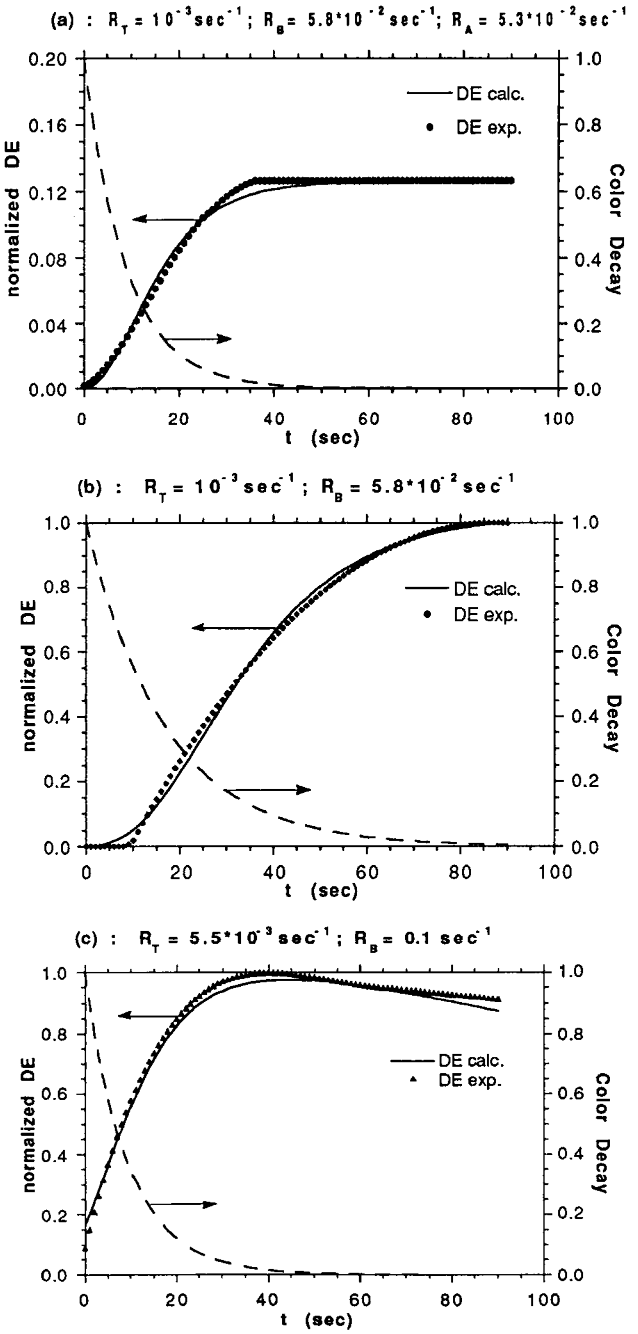


FIGURE 1 Normalized calculated and experimental DE and calculated color decay as a function of exposure time in spirooxazine/PMMA films. The calculated rate constants are shown on top of Figs. 2(a) - 2(c) for respective exposure configs. (a), (b), and (c).

The calculated DE responses were computed according Eq. (5) with constants of $L = 8\ \mu m$ and $\theta = 37.7°$ and the corresponding rate constants, as indicated on top of each figure. Furthermore, the modulation average and modulation depth were derived for each of the configurations from Eqs. (3) and (4), and substituted in Eq. (5). As evident, good agreement is obtained between theory and experiment, indicating the validity of our photokinetic equations. As shown, the calculated results in config. (c) were obtained with thermal and photochemical decoloration (bleaching) rate constants that were significantly higher than in configs. (a) and (b). This indicates that the simplified reaction scheme in Eq. (1) is not sufficient to explain our results. A more suitable reaction scheme may be given by

$$A \underset{R_{B1}(\lambda_B)\ ,\ R_{T1}}{\overset{R_A(\lambda_A)}{\rightleftarrows}} B_1 \underset{R_{B2}(\lambda_B)\ ,\ R_{T2}}{\overset{k_{T1}}{\rightleftarrows}} B_2 \quad , \tag{6}$$

where B_1 and B_2 are now two 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 k_{T1} is the thermal rate constant for the transformation from B_1 to B_2.

The results in Fig. 1 can be interpreted in terms of the relative populations of B_1 and B_2. In configs. (a) and (b), the initial exposure to the UV excitation beam alone, causes at steady state the more stable colored form B_2 to be dominantly populated. A following exposure to the visible recording beams causes decoloration to A, with the rate determining step being the transformation from B_2 to B_1. With config. (c), however, the initial exposure to all beams yields a mixture of all the forms, with a significant population of B_1. Therefore, the following exposure to the recording beams causes decoloration at a significantly increased rate, being mainly determined by the transformation from B_1 to A.

The identity of the two MC forms B_1 and B_2 cannot be derived with certainty from this investigation. We nevertheless suggest that B_1 and B_2 are stereoisomeric MC forms of different thermal and photochemical stability[2-6]. We believe that this is the most probable possibility among other alternatives, such as the influence of free volume distribution in the polymer matrix[2] or MC aggregate formation[2,7].

REFERENCES

1. V. Weiss, A. A. Friesem and V. A. Krongauz, Opt. Lett., 18(13), 1089 (1993).
2. H. Dürr and H. Bouas-Laurant (Eds.), Photochromism, Molecules and Systems, (Elsevier, 1990), chaps. 2, 8, 10, and 21.
3. J. C. Crano, W. S. Kwak and C. N. Welch, in Applied Photochromic Polymer Systems, C. B. McArdle (Ed.), (Blackie, Glasgow and London, 1992), chap. 2.
4. C. Schiele and G. Arnold, Tetrahed. Lett., 13, 1191 (1967).
5. C. Bohne, et al., J. Photochem. Photobiol. A: Chem., 66, 79 (1992).
6. S. Maeda, et al., in Chemistry of Functional Dyes, Vol. 2, (Proc. 2nd. Int. Symp. Chem. Functional Dyes, Kobe 1992), Z. Yoshida and Y. Shirota (Eds.), (Mita Press, Japan, 1993).
7. T. Hashida, J. Hibno, M. Suzuki, and Y. Kishimoto, in Ref. 13, p.345.
8. H. Kogelnik, Bell.Sys.Tech.J., 48, 2909 (1969).