PROCEEDINGS OF SPIE
SPIE—The International Society for Optical Engineering

Holographic Materials IV

T. John Trout
Chair/Editor

27 January 1998
San Jose, California

Sponsored by
SPIE—The International Society for Optical Engineering
IS&T—The Society for Imaging Science and Technology

Published by
SPIE—The International Society for Optical Engineering

Volume 3294

The papers appearing in this book comprise the proceedings of the meeting mentioned on the cover and title page. They reflect the authors' opinions and are published as presented and without change, in the interests of timely dissemination. Their inclusion in this publication does not necessarily constitute endorsement by the editors or by SPIE.

Please use the following format to cite material from this book:
Author(s), "Title of paper," in *Holographic Materials IV*, T. John Trout, Editor, Proceedings of SPIE Vol. 3294, page numbers (1998).

ISSN 0277-786X
ISBN 0-8194-2734-9

Published by
SPIE—The International Society for Optical Engineering
P.O. Box 10, Bellingham, Washington 98227-0010 USA
Telephone 360/676-3290 (Pacific Time) • Fax 360/647-1445

Printed in the United States of America.

STUDY OF THE QUANTUM YIELD AND MOLAR ABSORTIVITY FOR A DYE PHOTOBLEACHING IN A HOLOGRAPHIC RECORDING MATERIAL

Luis Carretero[1], Salvador Blaya[2], Antonio Fimia[2], Ricardo Mallavia[2], Roque F. Madrigal[2], Augusto Beléndez[3], Celia García[1].

1. Laboratorio de Óptica. Departamento Interuniversitario de Óptica. Universidad de Alicante, Apdo. 99. Alicante 03080 Spain, e-mail: luis@aclis.labopti.ua.es

2. Departamento de Ciencias Experimentales y Tecnología. Universidad Miguel Hernández. Av. Ferrocarril s/n Ed. Galia, Apdo. 03202, Elche (Alicante) Spain.

3. Departamento de Física, Ingeniería de Sistemas y Teoría de la señal. Universidad de Alicante. Apdo. 99. Alicante 03080 Spain.

ABSTRACT

The quantum efficiency and molar absorption coefficients of dyes are the responsible for holographic efficiency and sensitivity in a photopolymeric holographic recording material. These parameters have been obtained by fitting the experimental transmittance curves as function of time. For this using the mechanism of photoinitiation an analytical expression for the transmitted intensity in a photopolymerizable holographic material has been proposed, obtaining good agreement between theory and experience.

1. INTRODUCTION

In last years a great deal have been done on photopolymers as holographic recording materials,[1] caused by the stability if the generated holograms and the high diffraction efficiency reached. The dye's quantum yield, and the molar absorption coefficient are basic parameters that determine the photochemical behaviour of the holographic material. At the moment different studies of photoprocesses of photoinitiators trapped in transparent solid matrices have been carried out.[2-5]

A typical photopolymeric system consists in a polymeric matrix that supports monomers and photoinitiator system. Our material is composed by polyvinylalcohol as binder, acrylamide as monomer, an electron-donor (triethanolamine) and phenothiazine dyes like Methylene Blue, Azure-C, and Thionine. We propose a radical photopolymerization model which give us the possibility to obtain the constant of molar absorption for the different dyes studied and the quantum yield of radical generation, which it initiates polymerization reactions, using for this purpose the non-linear fit of the experimental transmittance curves as a function of time.

2. EXPERIMENTAL

The material used in these experiments is composed by acrylamide and triethanolamine as the coinitiator, provided both of them by SIGMA, photoinitiated with three different phenothiazine dyes (methylene blue, azure-C and thionine). These species are supported by a matrix of polyvinylalcohol (PVA) with molecular weight ≈ 25000. The photosensitive aqueous solution was prepared when over 50 ml of 10 % by weight of PVA, 2.5 ml of dye solution of the necessary concentration and 8 ml of 2.5 M of acrylamide and 1.5 M of triethanolamine were added. The film was prepared by coating the photosensitive solution over a 20x40 cm^2 glass (BK7) with a TLC coater provided by CAMAG allowing to dry for 20 h at normal conditions (60 % R. H. and 22 °C). The resulting thickness of the film was around 30 microns.

The experimental setup for measuring transmittance curves is shown in figure 1. A He-Ne laser of 633 nm wavelength, provided a linear polarized wave plane that it incides normal to the sample.

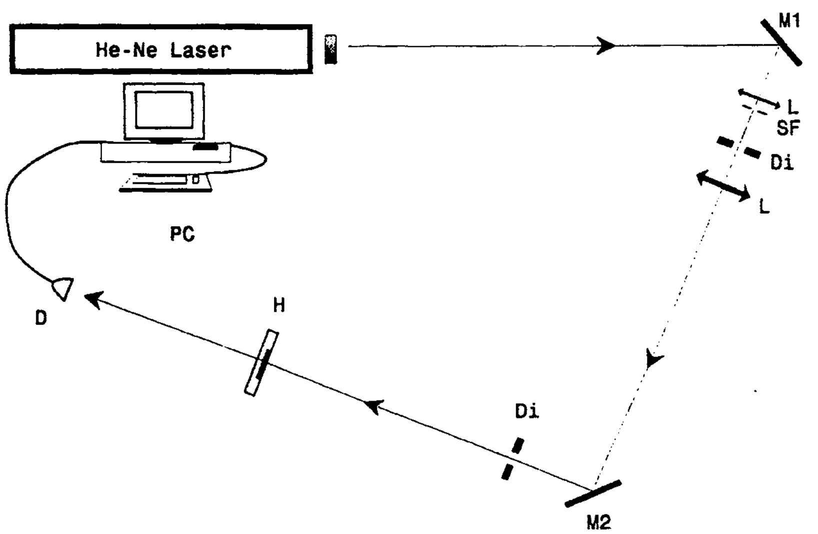

Figure 1. Experimental setup for the obtention of transmittance curves. SF: spatial filter. D: detector. L: Lens. Di: diaphragm. M: mirror. H: plate. PC: personal computer.

3. THEORETICAL MODEL

When a photopolymerizable material is irradiated at the wavelength of sensitization of the dye, a polymerization reaction is produced, whose proposed mechanism is showed in figure 2. Phenothiazine dyes when absorb light they produce excited forms that can be converted into radical molecules or return to the singlet state (non-excited). Through redox processes between excited dye molecules and amine produce a leuco form of the dye, in this case reduced-form, and the oxidized-form of the generated α-amino radicals that are capable to initiate the polymerization reaction. In this case the most possible termination process in the polymerization reaction is an unimolecular termination. Because we are working in a dry film which it has a high viscosity and the bimolecular termination is more difficult due to dependence of this constant with difussion.[6]

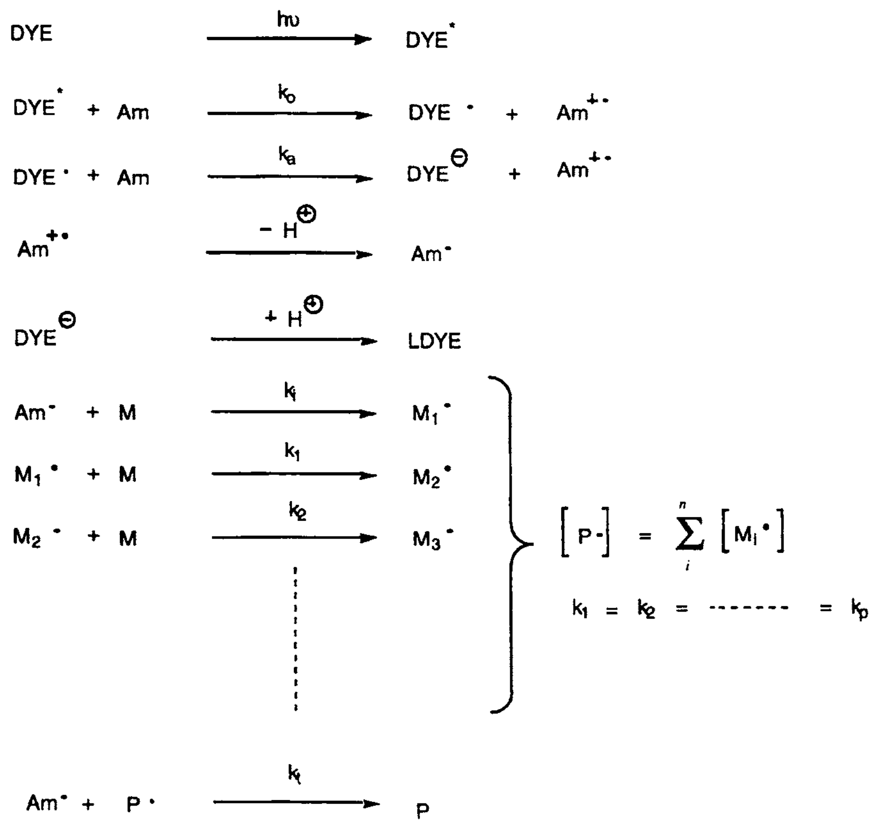

Figure 2. Scheme of the mechanism proposed for photopolymerization where DYE is the photoinitiator. Am: amine. P: polymer. M: monomer.

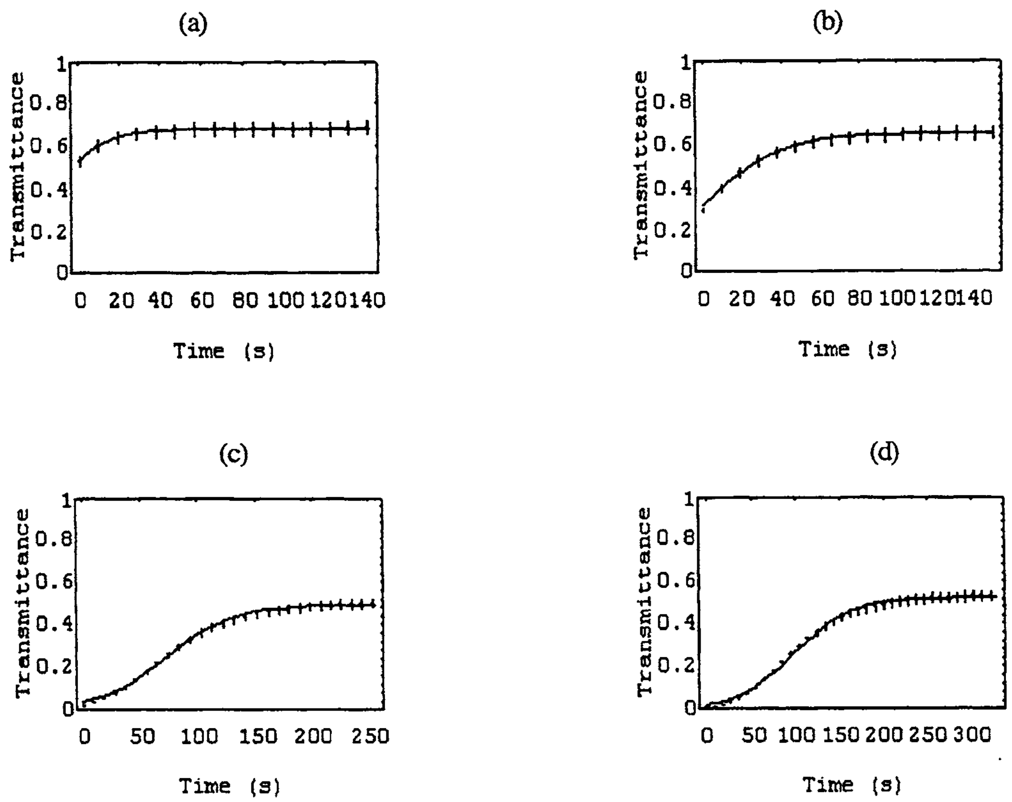

Figure 3: Experimental and fitted transmittance curves for materials with composition: AA: 0.335 M, PVA: 10%, TEA: 0.2 M and concentration of methylene blue: (a) 0.5×10^{-4} M; (b) 2.1×10^{-4} M; (c) 6.2×10^{-4} M; (d) 8.2×10^{-4} M. The initial intensity is 4.5 mW/cm^2.

A linear relationship between quantum yield and concentration of dye has been observed however molar absorption does not show this feature. At high concentrations of dye the quantum yield of generation of radicals is lesser, this fact can be related with the formation of dimeric species of the dye.[9]

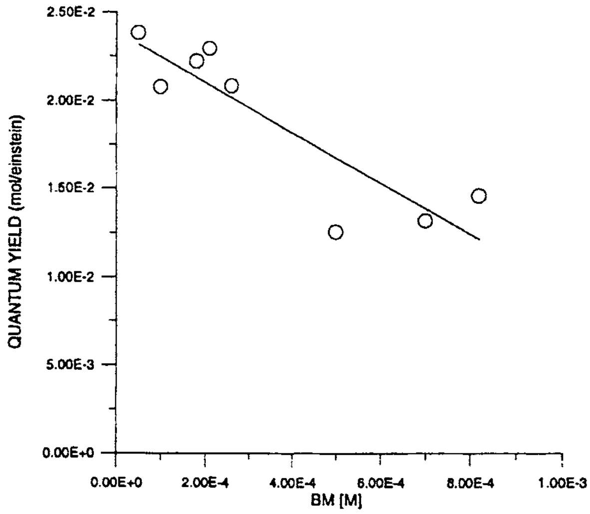

Figure 4. Variation of the quantum yield obtained with the concentration of initiator. The basic composition is: AA: 0.335 M, PVA: 10%, TEA: 0.2 M and the intensity is 4.5 mW/cm^2.

4.2 Intensity.

The effect of intensity in the obtained parameters is shown in figure 5. At low intensities the time required to bleach is higher, but the efficiency is practically constant. However the coefficient of molar absorption increases linearly with the incident intensity.

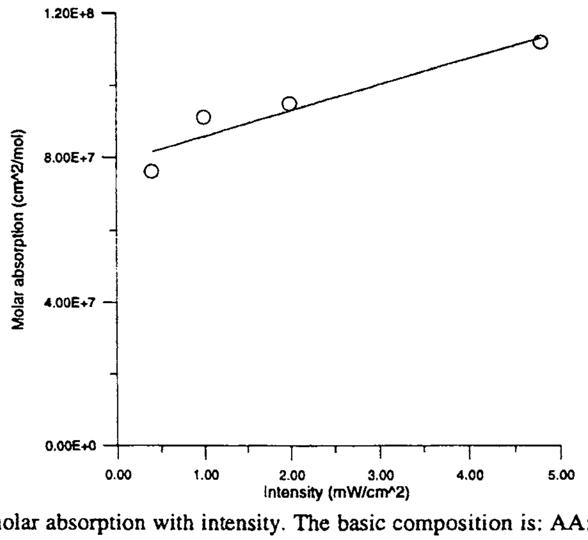

Figure 5. Variation of molar absorption with intensity. The basic composition is: AA: 0.335 M, PVA: 10%, TEA: 0.2 M and BM: 2.6x10^{-4} M.

4.3 Use of different phenothiazine dyes.

	ε (cm²/mol)	ϕ (mol/einstein)	Tsf
BM	$9.16x10^7$	0.021	0.655
AZURE-C	$6.03x10^7$	0.044	0.675
THIONINE	$4.47x10^7$	0.030	0.669

Table 1. Quantum yield, absorption coefficients and Tsf parameters for a wavelength of 633 nm obtained from non-linear fitting of transmittance curves. The basic composition is: AA: 0.335 M, PVA: 10%, TEA: 0.2 M, the concentration of each dye is $2.6x10^{-4}$ M and the intensity 4.1 mW/cm^2.

Three different dyes have been compared thionine (Th), Azure-C (Ac) and methylene blue (MB). Table 1 shows that quantum yield of azure-c is bigger than the obtained with methylene blue and thionine. These results agree with the fact that the maximum absorption of azure-C is closer to 633 nm than the others as can be seen in figure 6, where the absorption curves for different wavelengths obtained with a spectrophotometer has been represented. In this table the parameter Tsf is represented. It takes into account the light no transmitted due to scattering and reflections. This factor is similar for three dyes.

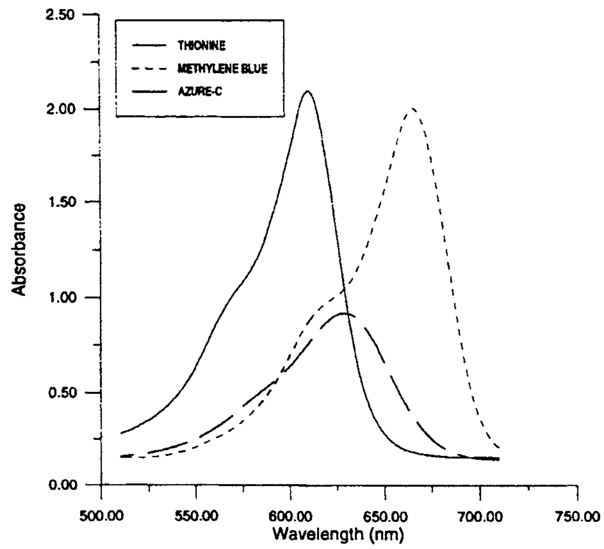

Figure 6. Absorption spectras for three dyes studied in a PVA film. The composition is: AA: 0.335 M, PVA: 10%, TEA: 0.2 M and DYE: $2.6x10^{-4}$ M.

5. CONCLUSIONS

Non-linear fit of the experimental measurements of the transmittance as a function of time using an analytical expression for transmittance obtained from a theoretical model, it has provided us the quantum yield and the molar absorption coefficient for different concentrations of methylene blue, intensities and three different phenothiazine dyes in the region of 633 nm. The knowledgement of these parameters is very important in the optimization process of holographic recording material, due to the dependence of sensitivity with quantum yield and molar absorption.

6. ACKNOWLEDMENTS

This work was supported by the *Direcció General d'Ensenyaments Universitaris i Investigació de la Generalitat Valenciana*, Spain (Project GV-C-CN-06-064-96) and to the commission interministerial de Ciencia y Tecnología (C.I.C.Y.T.) of Spain for financial support project MAT96-1767-E.

7. REFERENCES

1. R. Lessard, R. Changkakoti, G. Manivannan, "Holographic recording materials," *Processes Photoreact. Polym*, pp 307, (1995).

2.E. L. Simmons, "The photochemistry of solid layers. Reaction rates," *J. Phys. Chem.* **75**, pp 588-590 (1971).

3. C. Carré and D. J. Lougnot, "A photochemical study of the methylene blue/acrylamide system in view of its use for holographic recording under red illumination," *J. Chimie Phys.* **85**, pp 485-490 (1988).

4. N. Capolla and R. Lessard, "Real time bleaching of methylene blue or thionine sensitized gelatin," *Appl. Opt.* **30**, pp 1196-1200 (1991).

5. A. Dubois, M. Canva, A. Brun, F. Chaput and J. Boilot, "Photostability of dye molecules trapped in solid materices," *Appl. Opt.* **35**, pp 3193-3199 (1996).

6. G. Oster, N. Yang, "Photopolymerization of vinyl monomers," *Chem. Rev.* **68**, 125-151 (1968).

7. N. J. Turro, *Modern molecular photochemistry*, pp103 University Science of Books, (1991).

8. D. Marquardt, *SIAM J. Appl. Math.* **11**, 431-441 (1963)

9. C. S. H. Chen, "Dye-Sensitized photopolymerization. I. Polymerization of acrylamide by methylene blue-triethanolamine system," *J. Polym. Sci. A.* 1107-1125 (1965).